Impact of Microstructure on the Containment and Migration of CO₂ in Fractured Basalts

Project Number DE-FE0023382

Daniel Giammar, Mark Conradi, Sophia Hayes, and Phil Skemer
Washington University in St. Louis

Brian Ellis - University of Michigan

- Students and Postdocs: Jubilee Adeoye, Anne Menefee, Jinlei Cui, Erika Sesti, Rachel Wells, Wei Xiong, Yeunook Bae
- Technical Support: Helene Couvy
Presentation Outline

• Project Overview
• Carbon Sequestration in Fractured Basalts
• Research Approach
• Technical Status
  – Carbonate mineral formation in basalt fractures
  – Reactions of basalts with flowing CO$_2$-rich solutions
  – Estimate of carbon storage capacity in a basalt
• Summary and Opportunities
Sequestration in Mafic Formations

**Chemistry of Mineral Trapping**

\[
\begin{align*}
CO_2(\text{scf}) + H_2O &= 2H^+ + CO_3^{2-} \\
Mg_2SiO_4(s) + 4H^+ &= 2Mg^{2+} + H_4SiO_4 \\
Fe_2SiO_4(s) + 4H^+ &= 2Fe^{2+} + H_4SiO_4 \\
CaSiO_3(s) + 2H^+ + H_2O &= Ca^{2+} + H_4SiO_4 \\
Mg^{2+} + CO_3^{2-} &= MgCO_3(s) \\
Ca^{2+} + CO_3^{2-} &= CaCO_3(s) \\
Fe^{2+} + CO_3^{2-} &= FeCO_3(s)
\end{align*}
\]

- Mafic (Fe- and Mg-rich) rocks are formations with high mineral trapping capacity.
- Continued fracturing of the rock may be promoted by temperature and volume changes from reactions.

Carbonate precipitates on basalts after 854 days of reaction at 103 bar CO₂ and 100° C
Schaef et al., *Int. J. Greenhouse Gas Cont.*, 2010
Pilot-Scale Injections into Basalts

Basalts have the potential to rapidly sequester carbon in stable carbonate minerals.

Sidewall core from injection zone of Wallula, WA pilot well 24 months after injection of 1000 tons CO₂

Calcite in a core retrieved from the site of the 2012 CarbFix injection of CO₂-rich water into basalt in Iceland.

Snæbjörnsdóttir et al., *Int. J. Greenh. Gas Control*, 2017


Research Questions

- When and where to carbonate minerals form 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
Basalt Materials

Columbia River flood basalt (olivine rich)

Colorado basalt (serpentinized)

Grand Ronde basalt (silica and calcium rich)
Basalt Core Experiments – Dead End Fractures

- Six 600 mL pressure vessels
- Ultrapure water
- 100 °C or 150 °C
- 100 bar CO₂ in the headspace
- React up to 40 weeks, take core sample and liquid sample intermittently

- Straight groove pattern
- ~11 mm wide
- 90-100 µm depth
- Coat with epoxy
- Expose the top surface
Carbonate Formation in Dead-End Fractures

- Carbonate formation is spatially-localized.
- Reactive transport model output agrees with observations.
- Flood basalt is more reactive than serpentinized basalt (data not shown).
Carbonate Formation in Dead-End Fractures

- Carbonates form as early as six weeks.
- Growth of carbonates does not completely seal the fracture by 40 weeks.
- Carbonates are siderite (FeCO₃) and a Ca-Mg-Fe carbonate solids
- Precipitates are large enough to bridge the 100 µm fracture.
Grand Ronde Basalt (Relevant to Wallula)

- Cores in water
- 100 °C
- 100 bar CO₂
- 3.7% average porosity

- Carbonates (predominantly aragonite) form as early as six weeks.
- Large precipitates form in milled fracture and in vesicles.
• Carbonation rate = 1.24 ± 0.54 kg CO₂ / m³·y
• Filling all porosity (3.7%) would trap **47 kg CO₂ / m³**
• Could reach this capacity in **38 years**.
• Actual trend of mineral trapping with time is unknown.
Core Flooding Experiments

- Optical microscopy
- SEM/EDS
- Raman spectroscopy
- Pre-, post- CT scanning
## Core Flooding Experiments

<table>
<thead>
<tr>
<th>Condition</th>
<th>CB-1</th>
<th>CB-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>100°C</td>
<td>100°C</td>
</tr>
<tr>
<td>$P_{CO_2}$</td>
<td>20 MPa</td>
<td>20 MPa</td>
</tr>
<tr>
<td>Confining P</td>
<td>10 MPa</td>
<td>10 MPa</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1 mL/hr</td>
<td>1 mL/hr</td>
</tr>
<tr>
<td>Initial [NaHCO$_3$]</td>
<td><strong>6.3 mM</strong></td>
<td><strong>640 mM</strong></td>
</tr>
<tr>
<td>Initial pH</td>
<td>4.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Duration</td>
<td>10 days</td>
<td>12 days</td>
</tr>
</tbody>
</table>

[Image: Diagram of CO$_2$ injection and pH regulation]
Effluents from Core Flooding Experiments

The diagrams show the concentration of various ions (Ca, Mg, Fe, Si, K, Al) over reaction time (hours) for different temperatures (100°C, 6.3 mM and 100°C, 640 mM). The concentration is measured in parts per million (ppm). The data indicates a decrease in concentration over time, with some ions showing a more significant decrease than others.
Sample with 6.3 mM NaHCO₃ has gradients of alteration products.
Carbonates only observed in confined space outside of fracture.
Accomplishments to Date

- Identity, timing, and spatial location of carbonate mineral formation in dead-end fractures have been determined.
- Reactive transport model developed that provides very good simulations of carbonate mineral formation.
- Estimates of rates and capacity of sequestration in basalt.
  - trapping as stable carbonate solids
  - capacity of ~ 50 kg CO$_2$/m$^3$
  - could achieve this capacity within 40 years
Synergy Opportunities

- **Basalt Sequestration Projects:** share data and materials with others studying carbon sequestration in basalts.

- **Systems with Coupling of Reactions and Transport in Fractures:**
  - caprocks and well seals
  - hydraulic fracturing
  - enhanced geothermal systems

- **Modeling:** reactive transport model developed that can be adapted to different rocks and different settings.

- **Technique Development:** 4-D *in situ* X-ray computed tomography technique applied in collaboration with NETL in Morgantown.
Summary

– Key Findings
  • Fractured basalts have good mineral trapping capacities that can be achieved on time-scales of years.
  • Carbonate mineral formation is not self-limiting within 1 year; potential for it to be self-promoting is still being explored.
  • Good agreement between aqueous measurements, solid phase characterization, and model simulation.

– Lessons Learned
  • Integration of characterization techniques is critical.
  • Sequestration capacity depends on conditions and rock properties.

– Future Plans
  • Final flow-through experiments.
  • Experiments on fracture-propagation.
  • Prepare data packages for use in reactive transport modeling.
• Co-PI’s: Mark Conradi, Brian Ellis (Michigan), Sophia Hayes, and Phil Skemer.
• Students and Postdocs: Jubilee Adeoye, Anne Menefee, Jinlei Cui, Erika Sesti, Rachel Wells, Wei Xiong, Yeunook Bae
• Technical Support: Helene Couvy
Appendix

– Benefit to the Program
– Goals and Objectives
– Organization Chart
– Gantt Chart
– Bibliography
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.
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.
Organization Chart

NETL µCT Facility
- Dustin Crandall

UM Co-PI
- Ellis

CEE Ph.D Students
- Jubilee Adeoye
- Anne Menefee

EECE Ph.D Students
- Wei Xiong
- Yeunook Bae

Postdoc Researcher
- Rachel Wells

Chem. Ph.D Students
- Jinlei Cui

Postdoc Researcher
- Erika Sesti

DOE NETL
- Project Manager
  - Andrea McNemar

PI
- Giammar

WUStl Co-PIs
- Conradi, Hayes, Skemer

• Big Sky Partnership
• Steefel (LBNL)

DOE NETL Project Manager
- Andrea McNemar

NETL µCT Facility
- Dustin Crandall

UM Co-PI
- Ellis

CEE Ph.D Students
- Jubilee Adeoye
- Anne Menefee

EECE Ph.D Students
- Wei Xiong
- Yeunook Bae

Postdoc Researcher
- Rachel Wells

Chem. Ph.D Students
- Jinlei Cui

Postdoc Researcher
- Erika Sesti
## Gantt Chart

Received no-cost extension through March 31, 2018

### Task 1.0: Project Management & Planning

<table>
<thead>
<tr>
<th>Subtask</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Update PMP</td>
<td>01/07/15</td>
<td>02/06/15</td>
</tr>
<tr>
<td>Monthly &amp; Quarterly Reporting</td>
<td>10/01/14</td>
<td>09/30/17</td>
</tr>
<tr>
<td>Meetings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reports and Deliverables</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Task 2.0: Prepare and Characterize Basalt Samples

<table>
<thead>
<tr>
<th>Subtask</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural materials</td>
<td>10/01/14</td>
<td>12/23/14</td>
</tr>
<tr>
<td>Synthetic materials</td>
<td>01/01/15</td>
<td>04/02/15</td>
</tr>
<tr>
<td>Fracturing and characterization</td>
<td>01/01/15</td>
<td>06/30/15</td>
</tr>
<tr>
<td>Sample Characterization</td>
<td>01/01/15</td>
<td>01/01/16</td>
</tr>
</tbody>
</table>

### Task 3.0: Static Experiments

<table>
<thead>
<tr>
<th>Subtask</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screening in immersion</td>
<td>01/01/15</td>
<td>09/29/15</td>
</tr>
<tr>
<td>Systematic immersion expts</td>
<td>09/29/15</td>
<td>09/28/16</td>
</tr>
<tr>
<td>Confining pressure reactor test</td>
<td>04/01/15</td>
<td>10/01/15</td>
</tr>
<tr>
<td>Confining pres. systematic expts.</td>
<td>10/01/15</td>
<td>04/01/16</td>
</tr>
<tr>
<td>Confining pressure uCT exp.</td>
<td>04/01/16</td>
<td>09/28/16</td>
</tr>
<tr>
<td>In situ NMR prelim experiments</td>
<td>04/01/15</td>
<td>10/01/15</td>
</tr>
<tr>
<td>In situ NMR syst. experiments</td>
<td>10/01/15</td>
<td>04/01/16</td>
</tr>
<tr>
<td>Data integration and modeling</td>
<td>04/01/16</td>
<td>09/28/16</td>
</tr>
</tbody>
</table>

### Task 4.0: Core Flooding Experiments

<table>
<thead>
<tr>
<th>Subtask</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor assembly and testing</td>
<td>10/01/15</td>
<td>09/30/16</td>
</tr>
<tr>
<td>Experiments at UM</td>
<td>09/30/16</td>
<td>06/30/17</td>
</tr>
<tr>
<td>Flow-through with uCT</td>
<td>01/01/17</td>
<td>06/30/17</td>
</tr>
<tr>
<td>Flow-through NMR probe dev.</td>
<td>04/01/16</td>
<td>10/01/16</td>
</tr>
<tr>
<td>Flow-through NMR expts.</td>
<td>10/01/16</td>
<td></td>
</tr>
<tr>
<td>Data integration and modeling</td>
<td>01/01/17</td>
<td>01/01/18</td>
</tr>
</tbody>
</table>

---

**August 3, 2017**
Bibliography - Publications


6. Menefee, Anne; Li, Peiyuan; Giammar, Daniel; Ellis, Brian, Roles of transport limitations and mineral heterogeneity in carbonation of fractured basalts, accepted in *Environmental Science & Technology* in July 2017.

7. Wells, Rachel K., Wei Xiong, Daniel Giammar, and Philip Skemer, Dissolution and surface roughening of Columbia River flood basalt at geologic carbon sequestration conditions, accepted in *Chemical Geology* in July 2017.


3. Rachel K. Wells, Wei Xiong, Jubilee Adeoye, Anne Menefee, Brian Ellis, Philip Skemer and Daniel E. Giammar, Impact of dissolution and carbonate precipitation on carbon storage in basalt, American Geophysical Union Fall Meeting, December 12-16, 2016, San Francisco, California.


5. Anne H. Menefee, Peiyuan Li, Daniel E. Giammar, and Brian R. Ellis, CO2 storage in fractured basalt: Coupling experimental analyses with reactive transport modeling, Goldschmidt Conference, June 26 – July 1, 2016, Yokohama, Japan.


8. Wei Xiong, Rachel Wells, Philip Skemer, and Daniel Giammar, Carbonate mineral formation in fractured basalt at geologic carbon sequestration related conditions, 251st American Chemical Society National Meeting, March 13-17, 2016, San Diego, California.


13. Hayes, S.E., in situ NMR reveals conversion of 13CO2 to metal carbonates and pH monitoring for geosequestration studies, American Chemical Society Fall 2015 Meeting: Boston, MA, August 16-20. (invited)

14. Hayes, S.E., Euromar, Prague, Czechoslovakia, July 2015 “Materials for CO2 Capture and Sequestration Studied by 13C NMR” (invited talk and contributed poster)

