Impact of Microstructure on the Containment and Migration of CO$_2$ 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

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Transforming Technology through Integration and Collaboration
August 16-18, 2016
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
  - *In situ* solid-state $^{13}$C NMR tool
- 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.
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\textsubscript{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.
Sequestration in Mafic Formations

Chemistry of Mineral Trapping

\[ \text{CO}_2(\text{scf}) + \text{H}_2\text{O} = 2\text{H}^+ + \text{CO}_3^{2-} \]

\[ \text{Mg}_2\text{SiO}_4(\text{s}) + 4\text{H}^+ = 2\text{Mg}^{2+} + \text{H}_4\text{SiO}_4 \]

\[ \text{Fe}_2\text{SiO}_4(\text{s}) + 4\text{H}^+ = 2\text{Fe}^{2+} + \text{H}_4\text{SiO}_4 \]

\[ \text{CaSiO}_3(\text{s}) + 2\text{H}^+ + \text{H}_2\text{O} = \text{Ca}^{2+} + \text{H}_4\text{SiO}_4 \]

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

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3(\text{s}) \]

\[ \text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3(\text{s}) \]

- 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.
- Also applicable to \textit{ex situ} mineral carbonation in engineered reactors.

Carbonate precipitates on basalts after 854 days of reaction at 103 bar CO\textsubscript{2} and 100° C
Schaef et al., \textit{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.


Gislason and Oelkers, Science, 2014

www.or.is/en/projects/carbfix/
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 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
Flood Basalt 100°C, 100 bar 6 weeks

- Siderite (FeCO$_3$) formed 0.5 cm below the top.
- Precipitates are large enough to bridge the 100 µm fracture.
Serpentinized Basalt 100°C, 100 bar 6 weeks

pre-reaction

post-reaction

- Carbonate clusters located on red areas, which may be pyroxenes.
- The size of the clusters is ~200 um.
Spatial Distribution of Precipitates

- 100 µm step count
- Count if any precipitate is observed within square
- Resolution greater than 50 µm

Carbonate precipitates on the milled surface of flood basalt after 12 weeks

Carbonate formation is spatially localized with a maximum around 2 cm.
Reaction in an Induced Fracture

150 °C, 100 bar for 3 months
Flood basalt, 1-inch core

Precipitation within fracture:
- Did not fill fracture
- Bridged opening

Precipitate is < 400 μm
**In Situ $^{13}$C NMR Monitoring of Reaction**

Reaction of artificial rocks at 100 °C and 100 bar

- Basalt is much less reactive than pure forsterite.
- Evidence for bicarbonate production after 106 days with basalt.

$^{13}$C NMR static spin echo spectra

- Forsterite
  - Magnesite
  - $CO_2(aq)$
  - $HCO_3^-$

- Basalt:
  - 15% forsterite,
  - 20% diopside,
  - 65% labradorite
  - $CO_2(aq)$
  - $HCO_3^-$
  - 106 days
  - 33 days
  - 1 days
Basalt Core Experiments – Flow-Through

Experiment Conditions Initial pH
(CB/FB)-ES-1 45°C; ultrapure water 3.1
(CB/FB)-ES-2 100°C; ultrapure water 3.2
(CB/FB)-ES-3 100°C; 1.2 mM NaHCO₃ and 13.8 mM NaCl 3.6
Basalt Core Experiments – Flow-Through

- After initial high release, steady-state effluent concentrations achieved.
- Higher Mg and Ca at higher temperature and ionic strength.

**Flood Basalt Cores**

5 mL/hour flow

**Experimental Conditions**

<table>
<thead>
<tr>
<th>Experimental Condition</th>
<th>Temperature</th>
<th>Fluid Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES-1</td>
<td>45°C</td>
<td>ultrapure water</td>
</tr>
<tr>
<td>ES-2</td>
<td>100°C</td>
<td>ultrapure water</td>
</tr>
<tr>
<td>ES-3</td>
<td>100°C</td>
<td>1.2 mM NaHCO₃, 13.8 mM NaCl</td>
</tr>
</tbody>
</table>
Experimental Conditions

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ES-1</td>
<td>45°C</td>
<td>ultrapure water</td>
</tr>
<tr>
<td>ES-2</td>
<td>100°C</td>
<td>ultrapure water</td>
</tr>
<tr>
<td>ES-3</td>
<td>100°C</td>
<td>1.2 mM NaHCO₃, 13.8 mM NaCl</td>
</tr>
</tbody>
</table>

- Effluent pH calculated based on CO₂ solubility and charge balance.
- Solution has not become saturated with respect to any minerals.
- Siderite (FeCO₃) is the mineral closest to saturation.
X-ray Computed Tomography Evaluation of Fracture Volume Change

- X-ray CT imaging clearly indicates an increase in fracture volume.
- Effluent elemental analysis suggests 0.014 cm³ increase from an initial fracture volume of approximately 0.023 cm³.
- Increase comes primarily from dissolution of olivine, pyroxene, and plagioclase.
High Pressure NMR Hardware

- Can detect dissolved CO$_2$ circulating through the NMR probe.
- In Year 3 we will evaluate reactions of CO$_2$-rich solutions with artificial basalts.

Test Conditions:
- Pressure = 50 bar
- Flow Rate: 0.1 mL/min
- T = 25 °C
Accomplishments to Date

– Identity and spatial location of carbonate mineral formation in dead-end fractures have been determined.
– Quantification of the relative reactivity of two different basalts over a range of conditions.
– Development of a laboratory-scale experimental systems for evaluating CO$_2$-rich fluid interactions with basalts.
  • Flow-through fractured basalts held under confining pressure.
  • $^{13}$C NMR hardware for tracking reaction progress *in situ* under both static and advective flow conditions.
Synergy Opportunities

– **Basalt Sequestration Projects:** share data and materials with others studying carbon sequestration in basalts.
  - Work with Grand Ronde Basalt facilitated by Todd Schaef (PNNL)
  - Ryan Pollyea and Sally Benson project on CO$_2$ transport in fractured basalts.
  - Our “Sample Library of Natural and Artificial Basalts” is available on EDX.

– **Other Sequestration Projects:** examine impacts of fracture microstructure on CO$_2$ behavior in other reactive materials.

– **Modeling:** generate a rich dataset that can be used to evaluate reactive transport and geomechanical models.

– **Technique Sharing:** we have unique abilities (e.g., solid state $^{13}$C NMR) that can be brought to other groups.
Summary

– Key Findings
  • Carbon mineralization in fractured basalts can result in mineral trapping on time-scales of years or less.
  • Consistent results from batch and flow-through experiments.
  • Spatially-localized siderite formation occurs in dead-end fractures.

– Lessons Learned
  • Improved methods for creating induced fractures.
  • New fracture morphology to simultaneously evaluate reactions in fractures with advective flow and in dead-end fractures.

– Future Plans
  • Completion of the large set of batch experiments.
  • Flow-through experiments with in situ CT imaging at NETL.
  • Experiments using the flow-through NMR probe.
  • 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

http://pages.wustl.edu/fracturedbasalts
Appendix

– Organization Chart
– Gantt Chart
– Bibliography
Organization Chart

DOE NETL
Project Manager
Andrea McNemar

PI
Giammar

WUSl Co-PIs
Conradi, Hayes, Skemer

• Big Sky Partnership
• Steefel (LBNL)

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

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

• Anne H. Menefee, Peiyuan Li, Daniel E. Giammar, and Brian R. Ellis, CO$_2$ storage in fractured basalt: Coupling experimental analyses with reactive transport modeling, *Goldschmidt Conference*, June 26 – July 1, 2016, Yokohama, Japan.

• Jubilee Adeoye, Anne H. Menefee, Wei Xiong, Rachel K. Wells, Philip A. Skemer, Daniel E. Giammar, and Brian R. Ellis, Reaction products and evolution of permeability during carbon sequestration in fractures of unaltered and serpentinized basalt, *Goldschmidt Conference*, June 26 – July 1, 2016, Yokohama, Japan.


• 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.

• Wells, R., Xiong, W., Bae, Y., Sesti, E., Skemer, P., Giammar, D., Conradi, M., Ellis, B. and S. Hayes, Dissolution-precipitation reactions and permeability evolution from reactions of CO$_2$-rich aqueous solutions with fractured basalt, American Geophysical Union Fall Meeting, September 12-16, 2015, San Francisco, California.

• Hayes, S. NMR$^2$ meeting, Albuquerque, NM. Oct. 2015 “NMR and in the Compton Basement—a Presentation in Honor of Prof. Mark S. Conradi” (invited talk).

• Xiong, W., Wells, R., Skemer, P., and D. Giammar, Carbonate mineral formation in fractured basalt at geologic carbon sequestration related conditions, Mid-America Environmental Engineering Conference, October 24, 2015, Columbia, Missouri.

• Giammar, D., Conradi, M., Hayes, S., Skemer, P., and Ellis, B. Impact of microstructure on the containment and migration of CO2 in fractured basalts, Carbon Storage R&D project Review Meeting, August 18-20, 2015, Pittsburgh, Pennsylvania.

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

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

