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

Project Number DE-FE0023382

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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_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

$$CO_{2(scf)} + H_2O = 2H^+ + CO_3^{2-}$$

$$Mg_2SiO_{4(s)} + 4H^+ = 2Mg^{2+} + H_4SiO_4$$

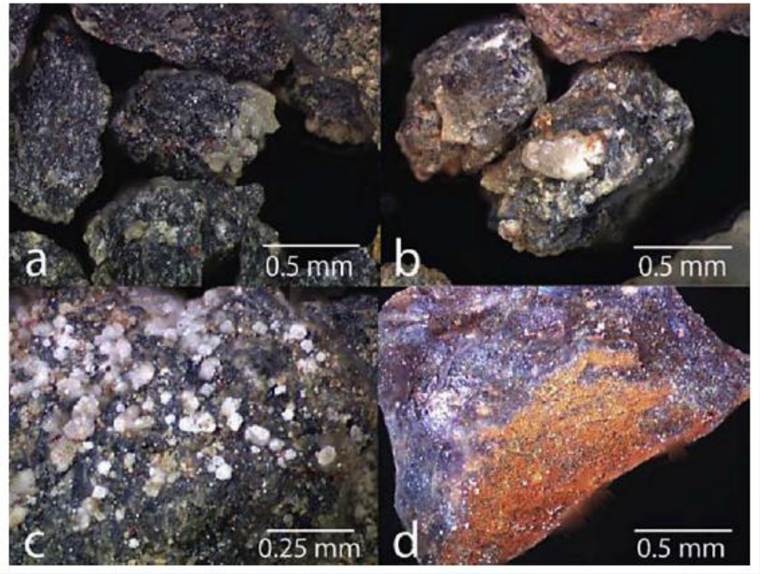
$$Fe_2SiO_{4(s)} + 4H^+ = 2Fe^{2+} + H_4SiO_4$$

$$CaSiO_{3(s)} + 2H^+ + H_2O = Ca^{2+} + H_4SiO_4$$

$$Mg^{2+} + CO_3^{2-} = MgCO_{3(s)}$$

$$Ca^{2+} + CO_3^{2-} = CaCO_{3(s)}$$

$$Fe^{2+} + CO_3^{2-} = FeCO_{3(s)}$$

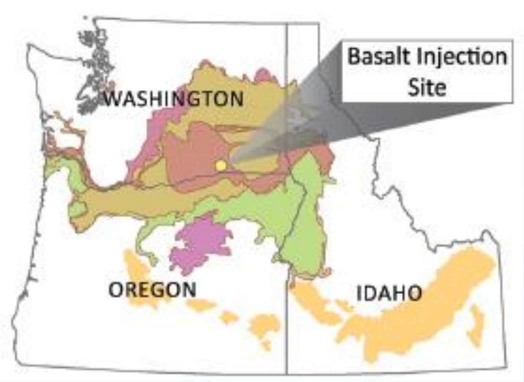


Carbonate precipitates on basalts after 854 days of reaction at 103 bar CO_2 and 100° C
Schaef et al., *Int. J. Greenhouse Gas Cont.,* 2010

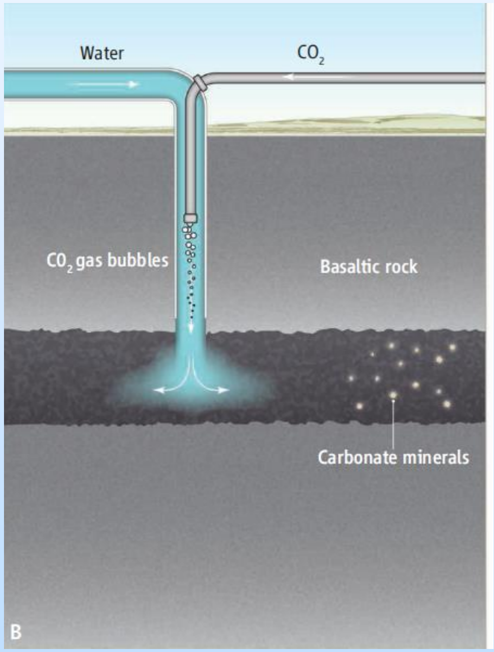
- Mafic (Fe- and Mg-rich) rocks are formations with high mineral trapping capacity.
- Continued fracturing of the rock may be promoted by temperature and volume changes from reactions.
- Also applicable to *ex situ* mineral carbonation in engineered reactors.

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.

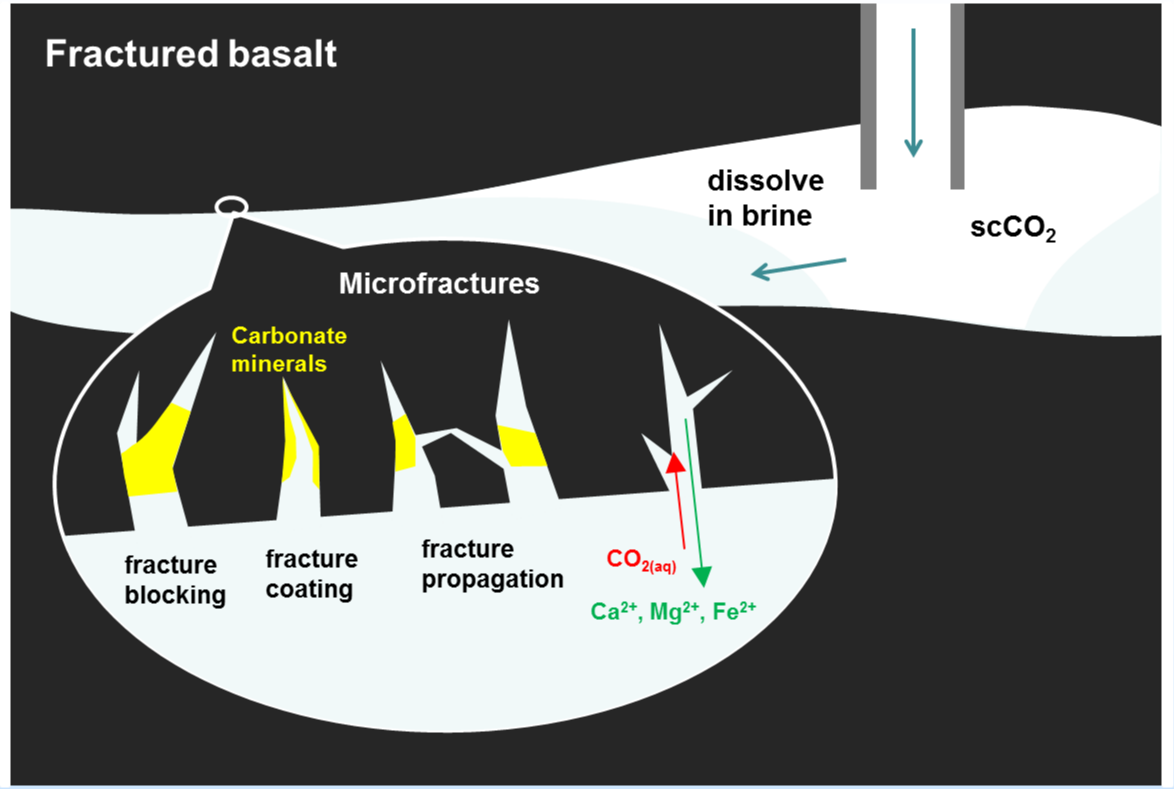
80% of injected CO_2 mineralized within 1 year.

Matter et al, *Science,* 2016

Washington University in St. Louis

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

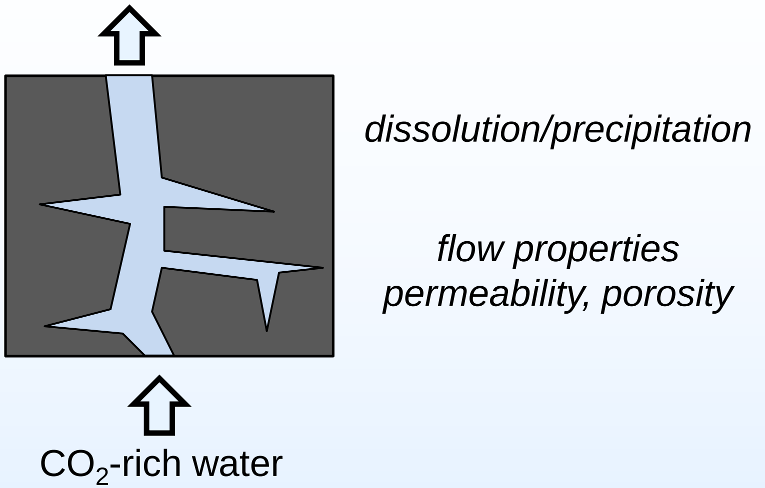
- Natural and artificial rocks
- Varying composition and fracture structure

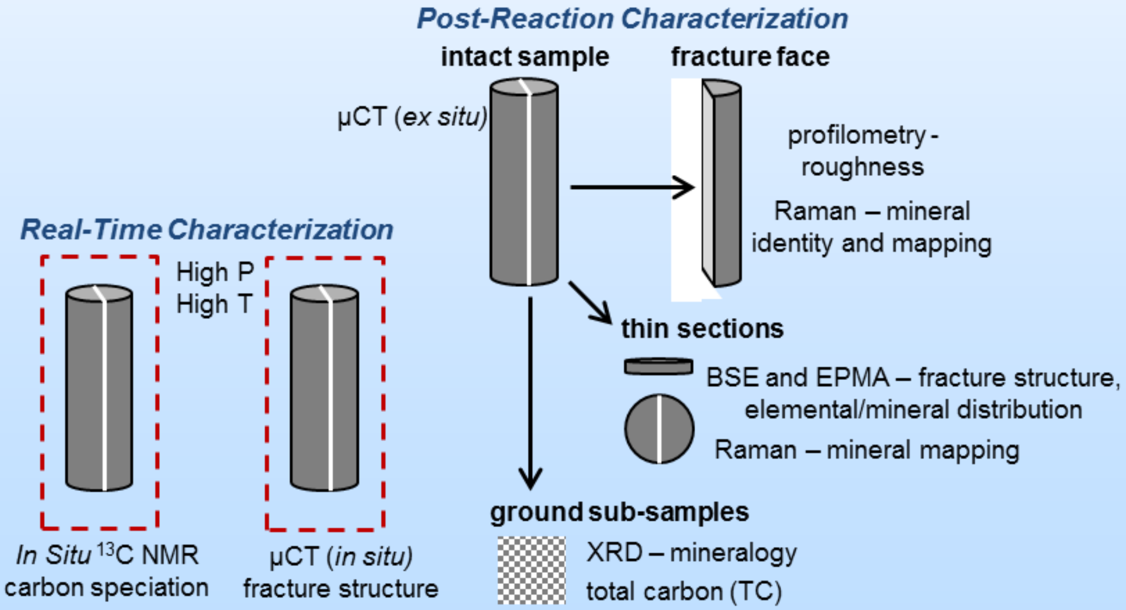
Bench-Scale Experiments

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

Characterization

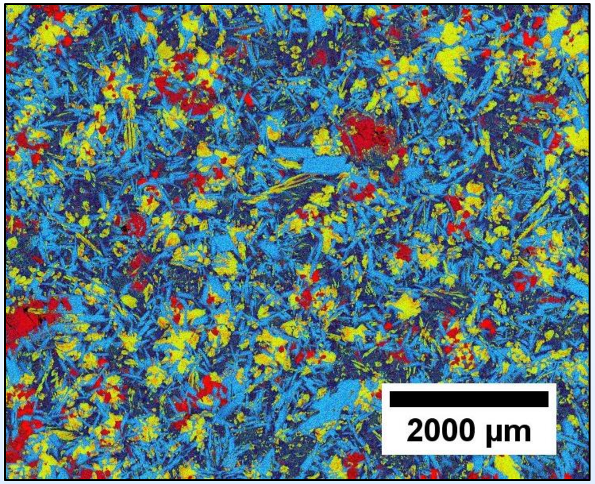
- Pre- and post-reaction
- *Ex situ* and *in situ* techniques.



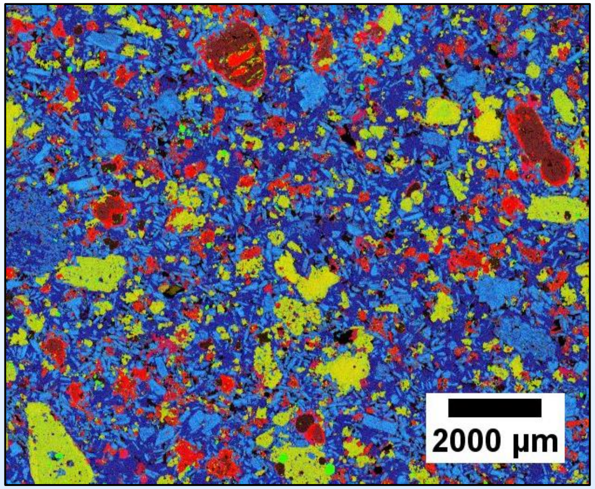


Basalt Materials

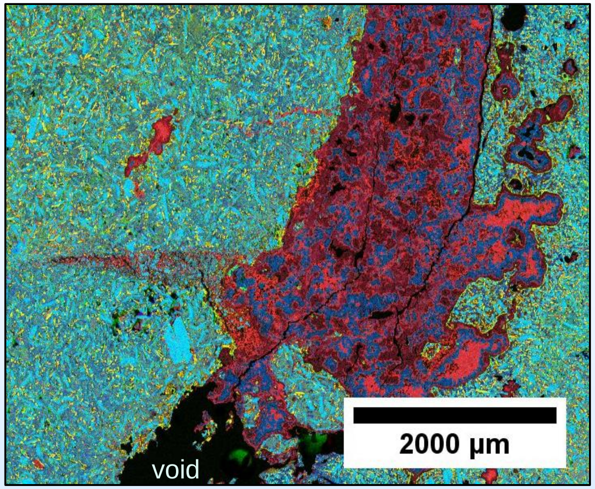
Columbia River flood basalt
(olivine rich)

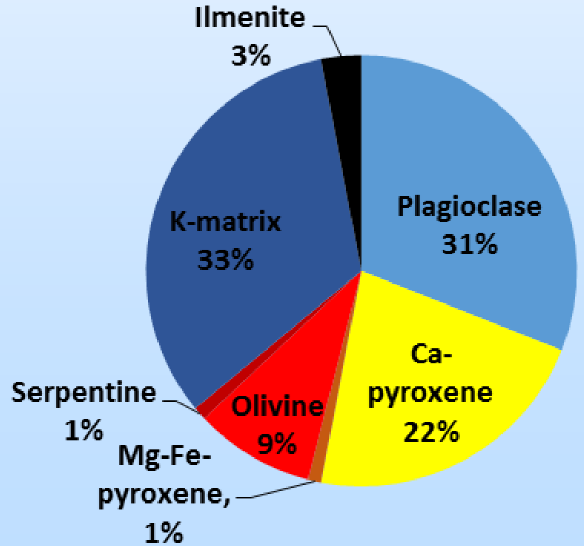


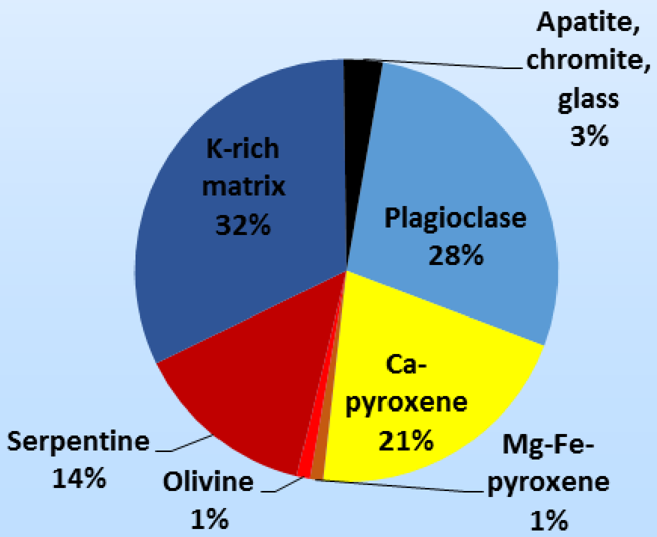
Colorado basalt
(serpentinized)

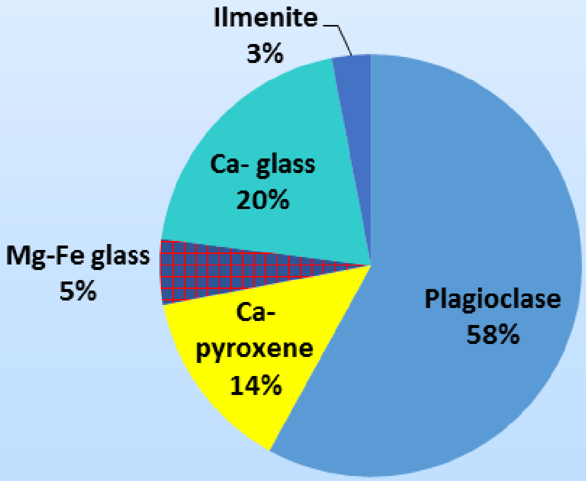


Grand Ronde basalt
(silica rich)



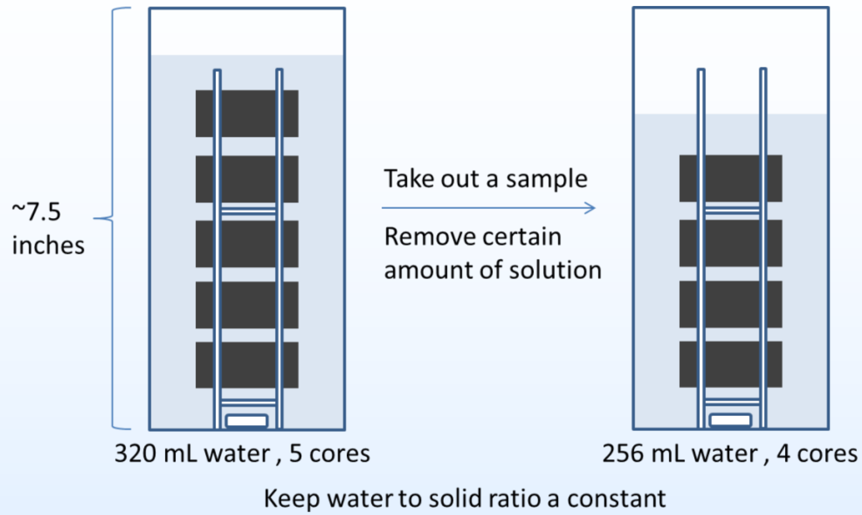






Basalt Core Experiments – Dead End Fractures

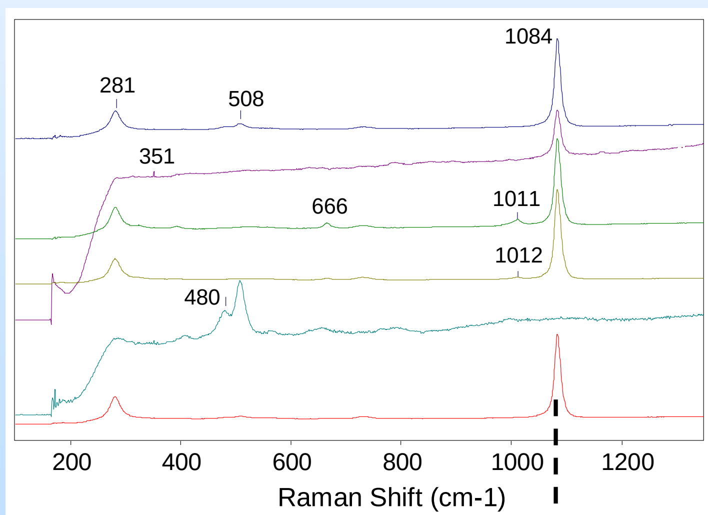
- Six 600 mL pressure vessels
- Ultrapure water
- 100 °C or 150 °C
- 100 bar CO_2 in the headspace
- React up to 40 weeks, take core sample and liquid sample intermittently



- Straight groove pattern
- ~11 mm wide
- 90-100 µm depth
- Coat with epoxy
- Expose the top surface

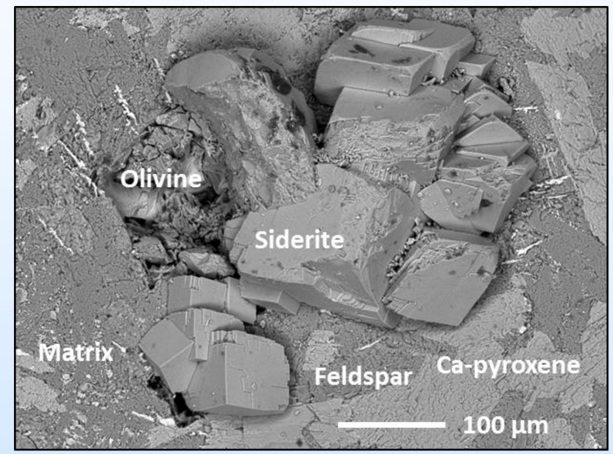
Flood Basalt 100°C, 100 bar 6 weeks

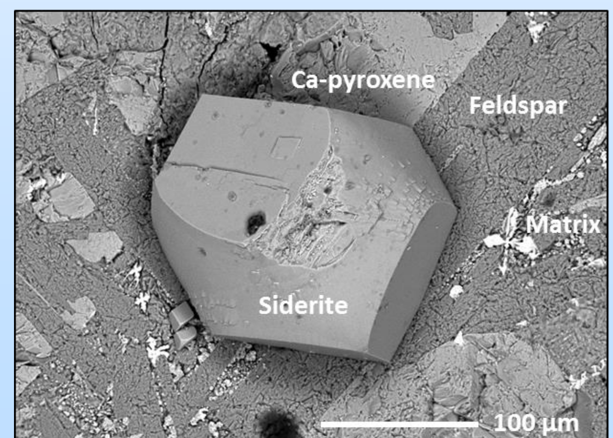
post-reaction



carbonate peak

- Siderite ($FeCO_3$) formed 0.5 cm below the top.
- Precipitates are large enough to bridge the 100 µm fracture.



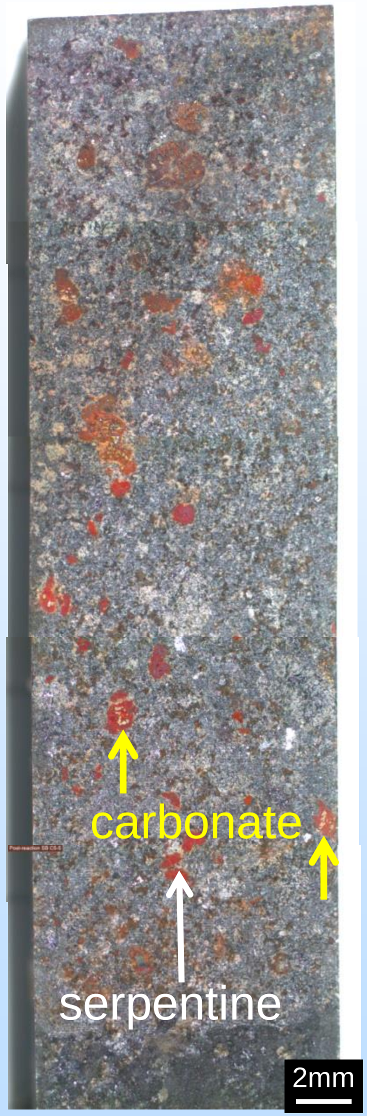


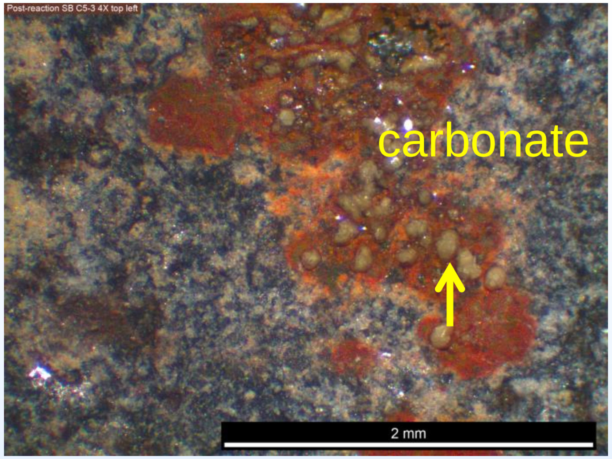
Serpentinized Basalt 100°C, 100 bar 6 weeks

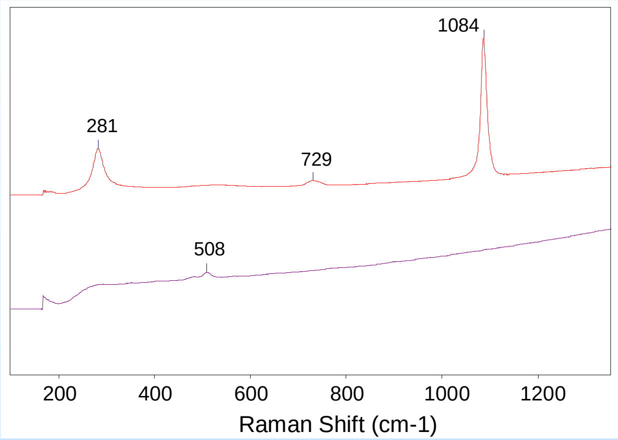
pre-reaction

post-reaction

iron oxides

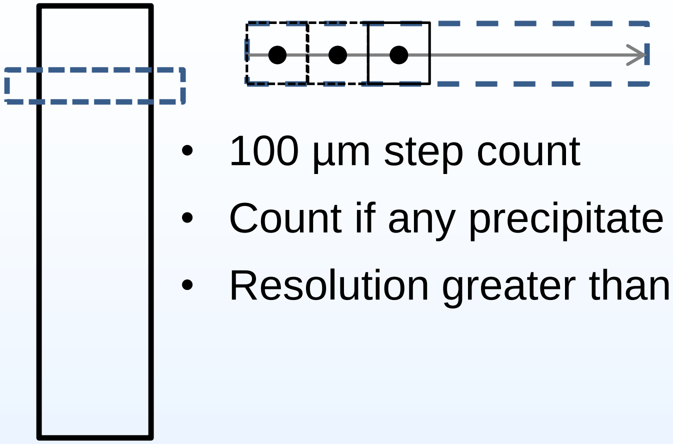




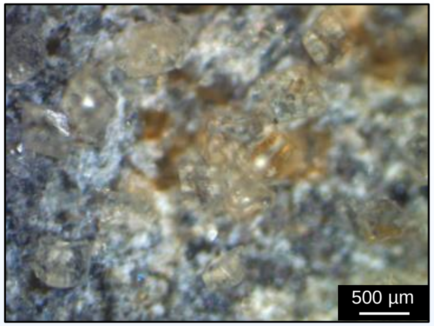


- Carbonate clusters located on red areas, which may be pyroxenes.
- The size of the clusters is ~200 um.

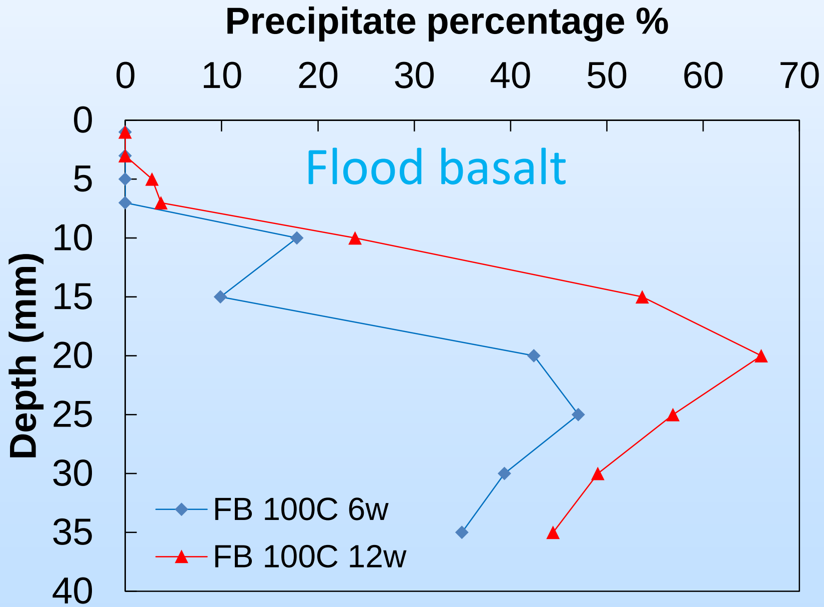
Spatial Distribution of Precipitates

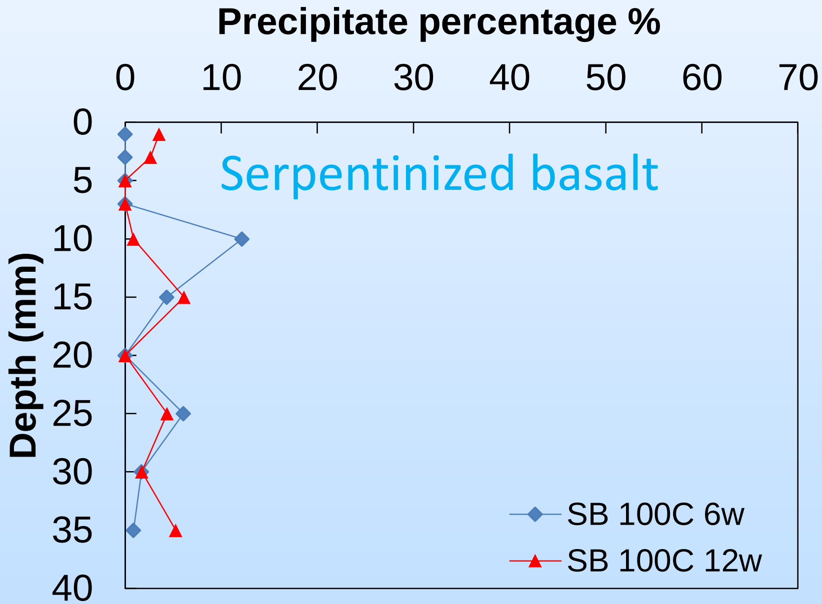


- 100 µm step count
- Count if any precipitate is observed within square
- Resolution greater than 50 µm



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



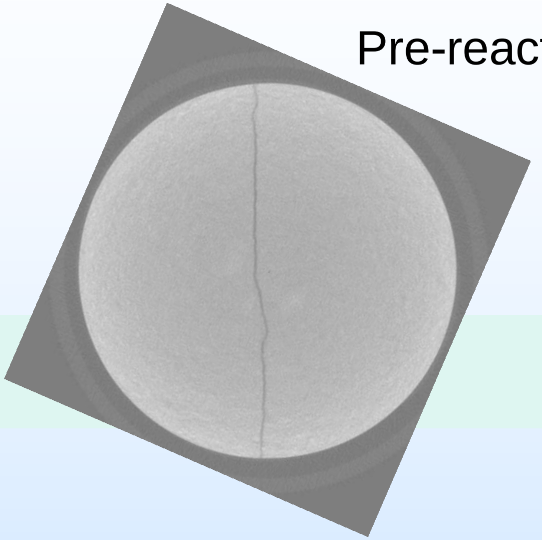


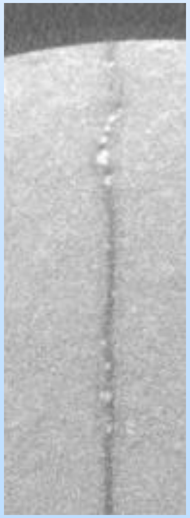
Carbonate formation is spatially localized with a maximum around 2 cm.

Reaction in an Induced Fracture

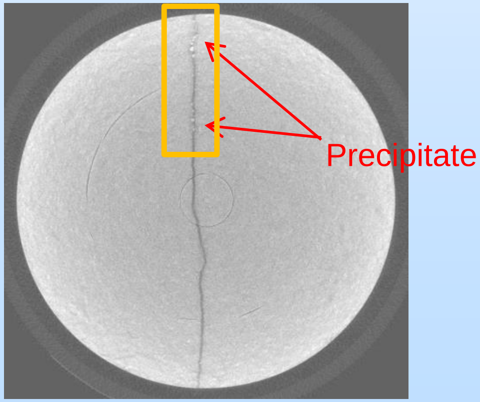
150 °C, 100 bar for 3 months
Flood basalt, 1-inch core

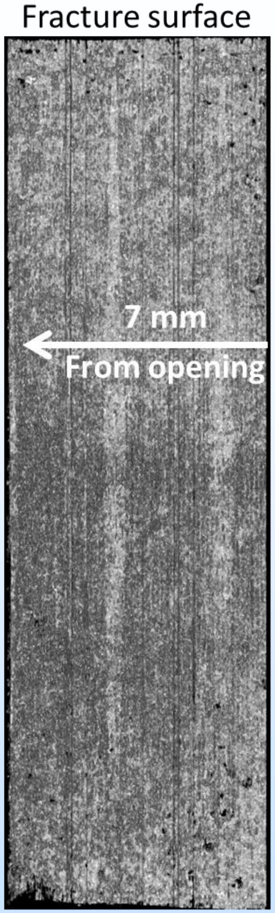
Pre-reaction

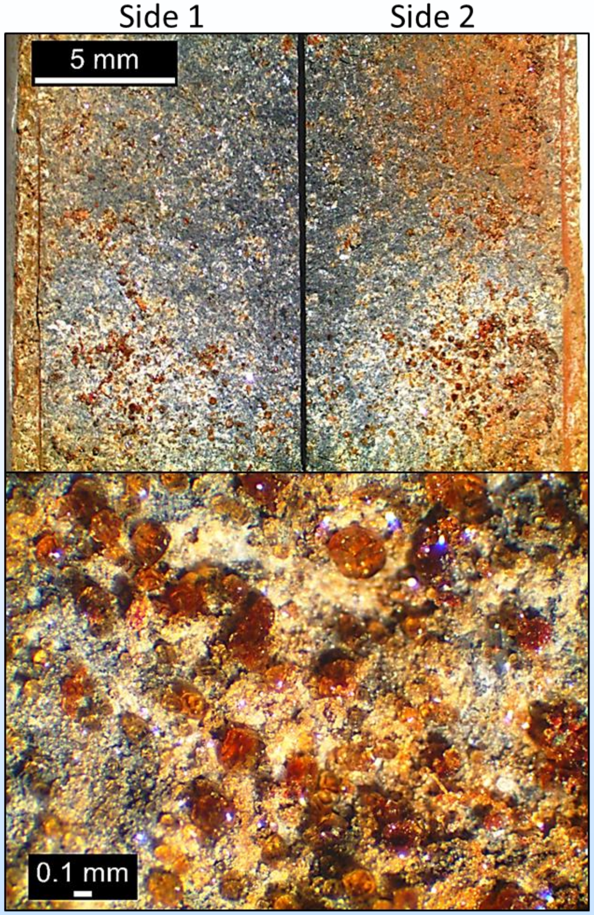




Post-reaction





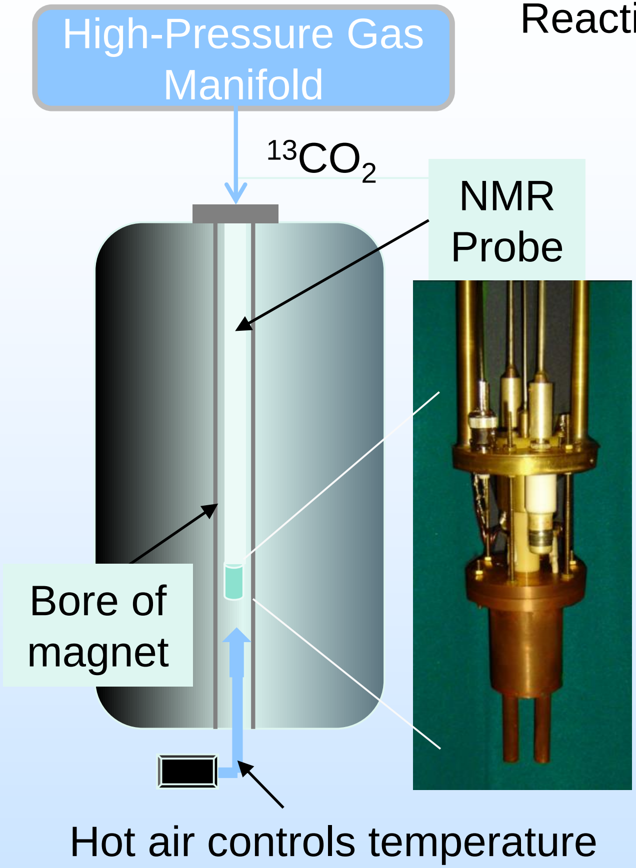


Precipitate is < 400 μm

Precipitation within fracture:

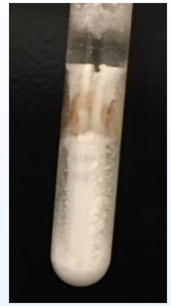
- Did not fill fracture
- Bridged opening

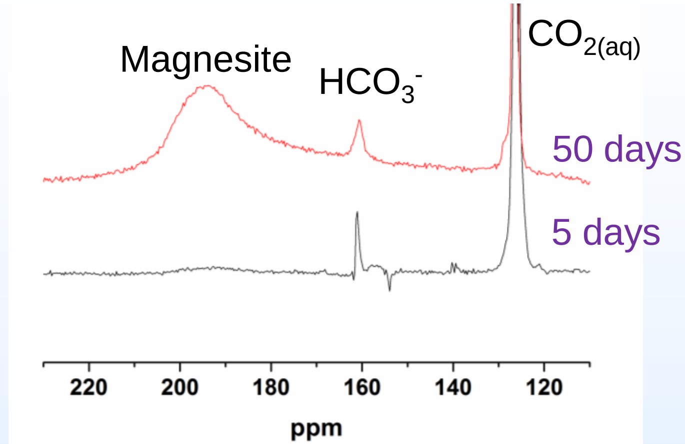
In Situ ^{13}C NMR Monitoring of Reaction



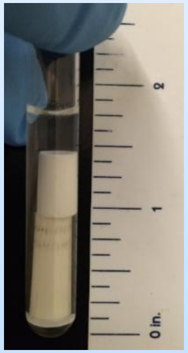
Reaction of artificial rocks at at 100 °C and 100 bar

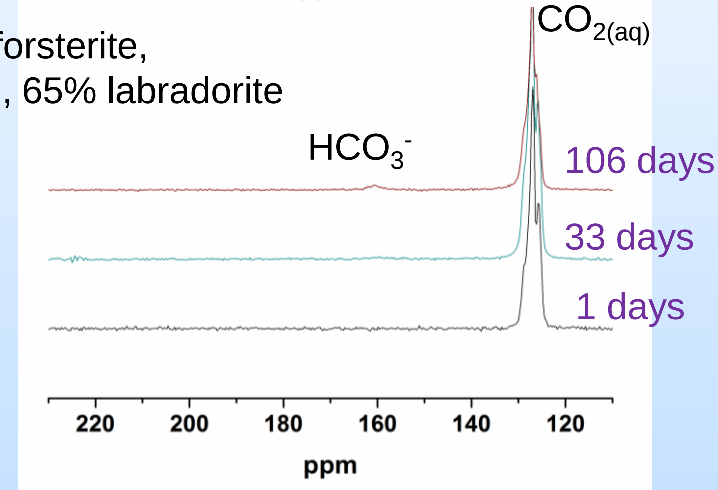
forsterite





basalt: 15% forsterite, 20% diopside, 65% labradorite

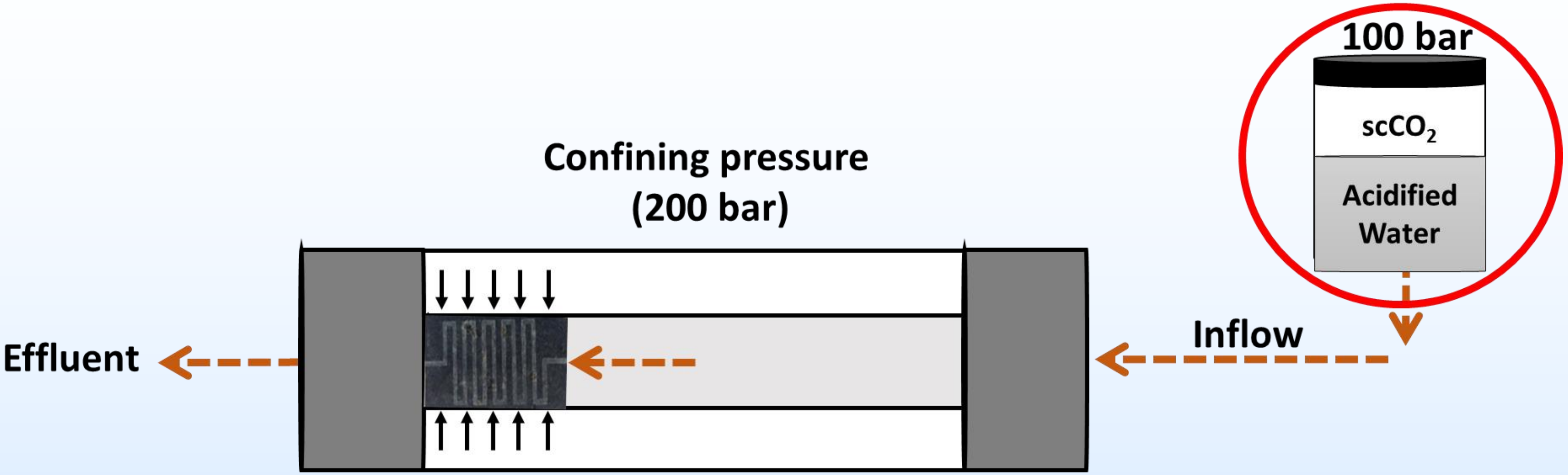


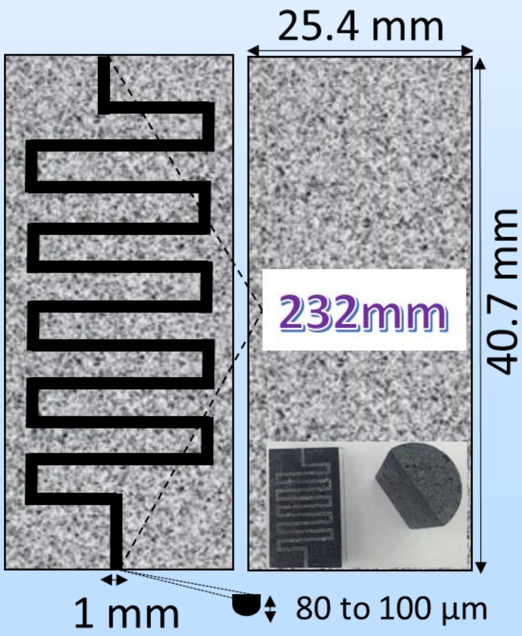


- Basalt is much less reactive than pure forsterite.
- Evidence for bicarbonate production after 106 days with basalt.

^{13}C NMR static spin echo spectra

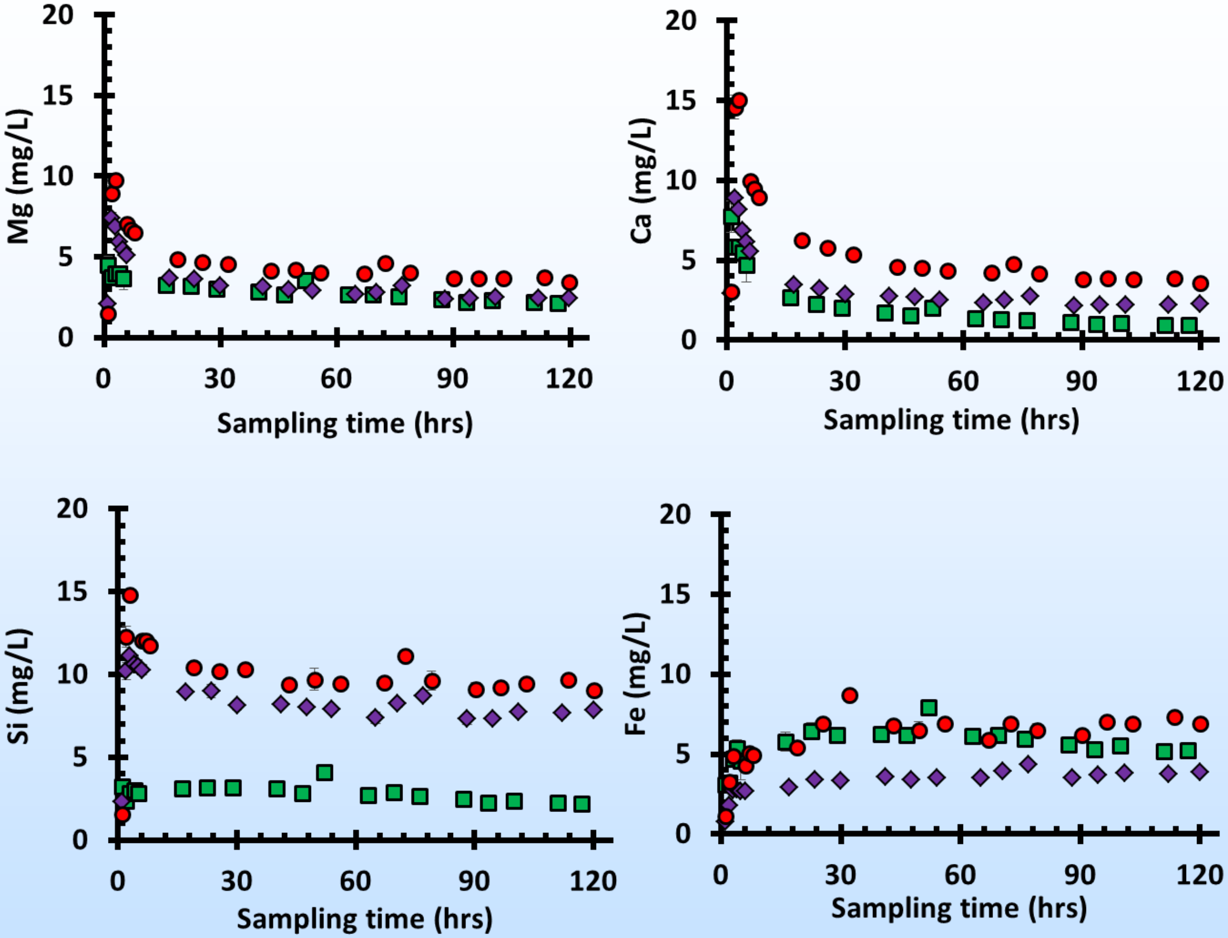
Basalt Core Experiments – Flow-Through





Experiment	Conditions	Initial pH
(CB/FB)-ES-1	45^{o}C; ultrapure water	3.1
(CB/FB)-ES-2	100^{o}C; ultrapure water	3.2
(CB/FB)-ES-3	100^{o}C; 1.2 mM $NaHCO_3$ and 13.8 mM NaCl	3.6

Basalt Core Experiments – Flow-Through

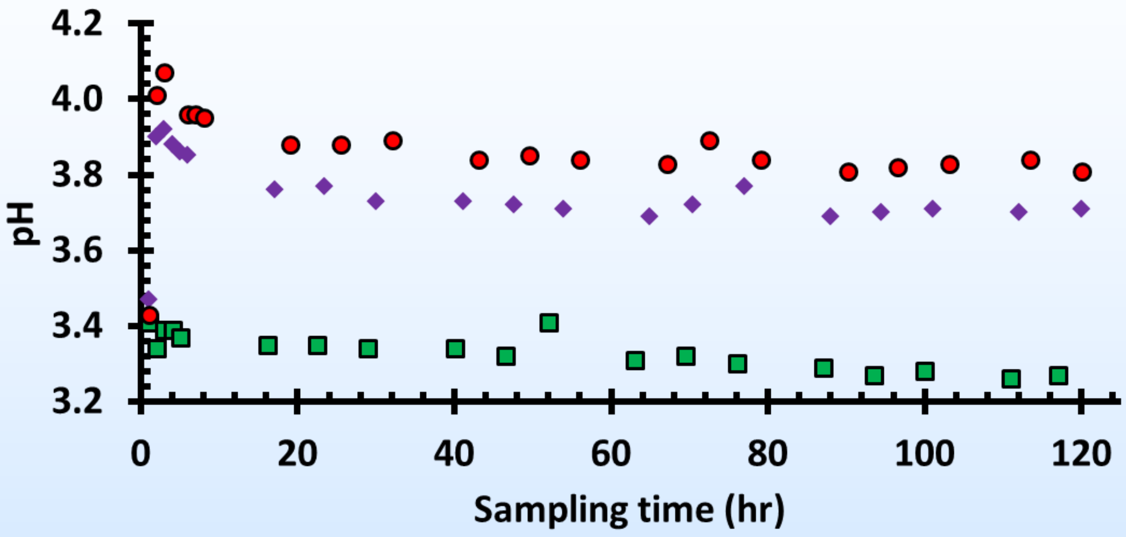


Flood Basalt Cores
5 mL/hour flow

Experimental Conditions		
ES-1	45°C	ultrapure water
ES-2	100°C	ultrapure water
ES-3	100°C	1.2 mM $NaHCO_3$ 13.8 mM NaCl

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

Basalt Core Experiments – Flow-Through



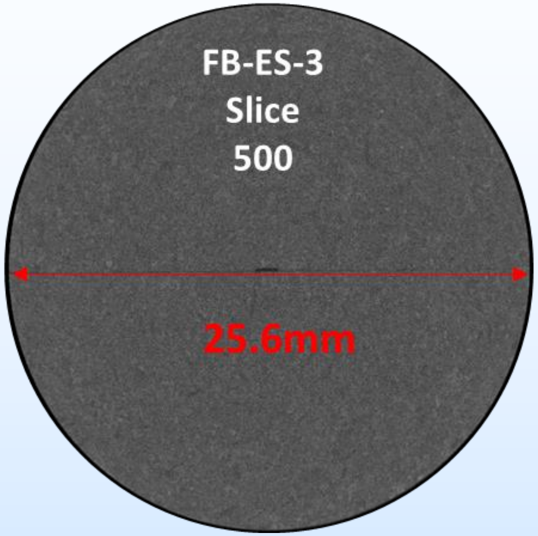
Flood Basalt Cores
5 mL/hour flow

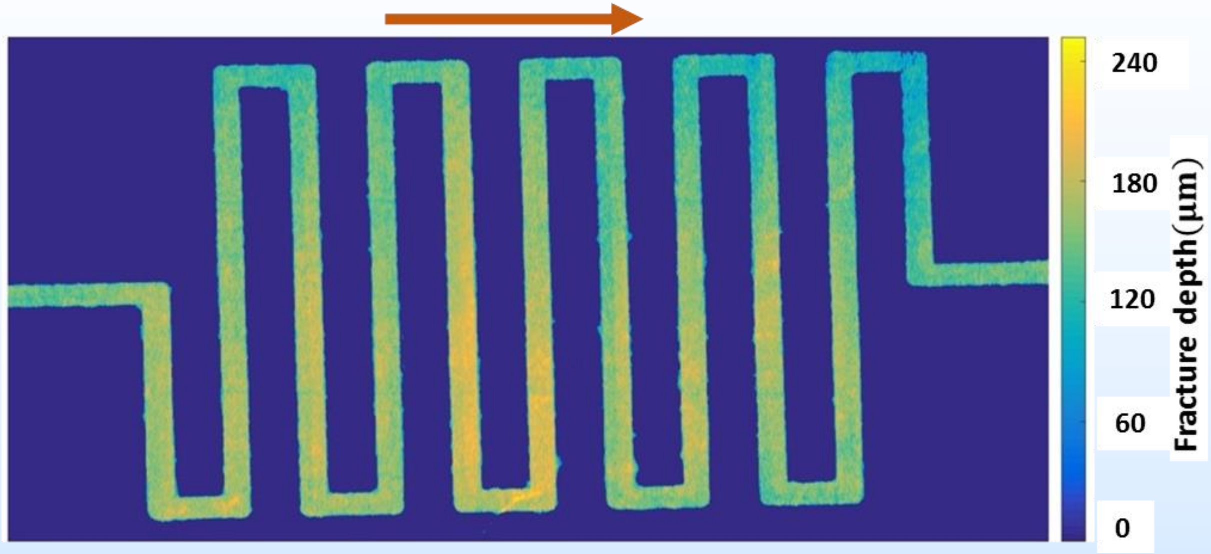
Experimental Conditions		
ES-1	45°C	ultrapure water
ES-2	100°C	ultrapure water
ES-3	100°C	1.2 mM $NaHCO_3$ 13.8 mM NaCl

- Effluent pH calculated based on CO_2 solubility and charge balance.
- Solution has not become saturated with respect to any minerals.
- Siderite ($FeCO_3$) is the mineral closest to saturation.

Basalt Core Experiments – Flow-Through

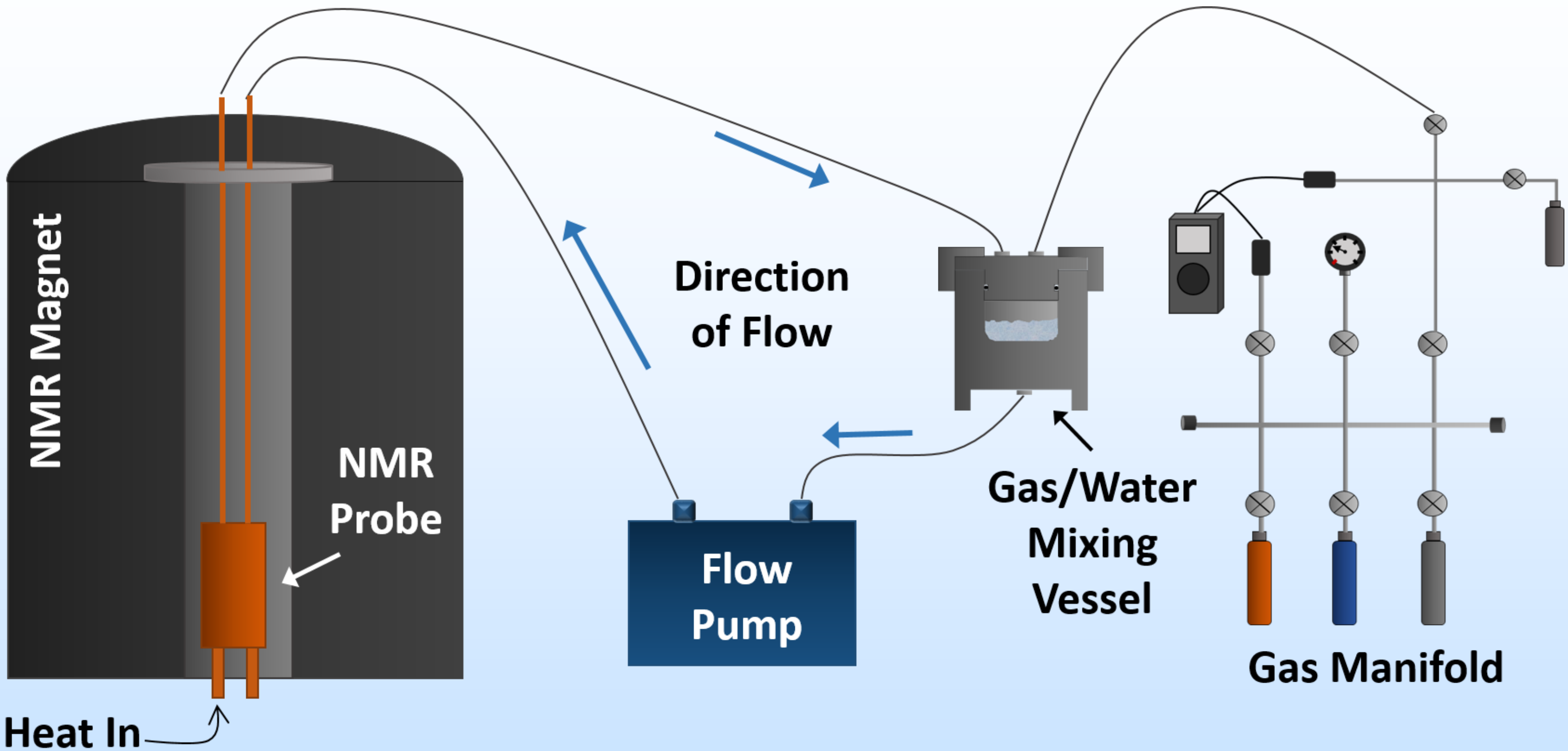
X-ray Computed Tomography Evaluation of Fracture Volume Change



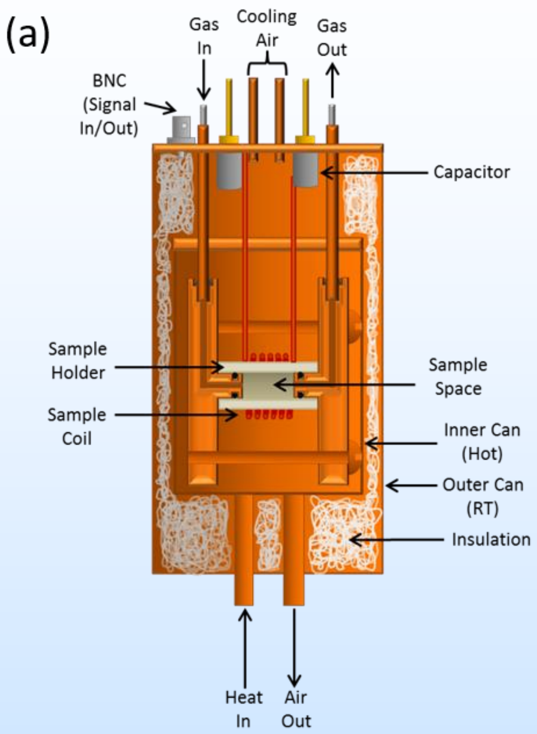


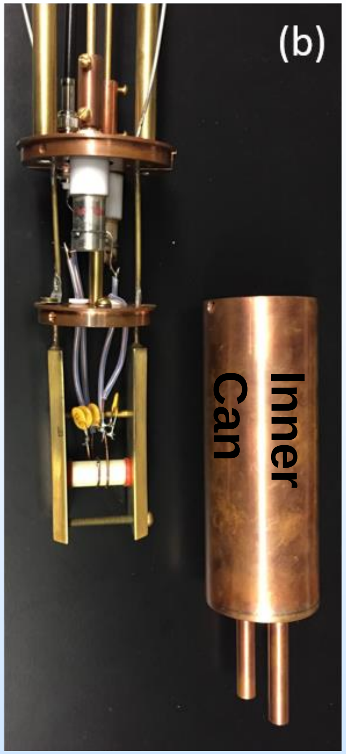
- X-ray CT imaging clearly indicates an increase in fracture volume.
- Effluent elemental analysis suggests 0.014 cm^3 increase from an initial fracture volume of approximately 0.023 cm^3.
- Increase comes primarily from dissolution of olivine, pyroxene, and plagioclase.

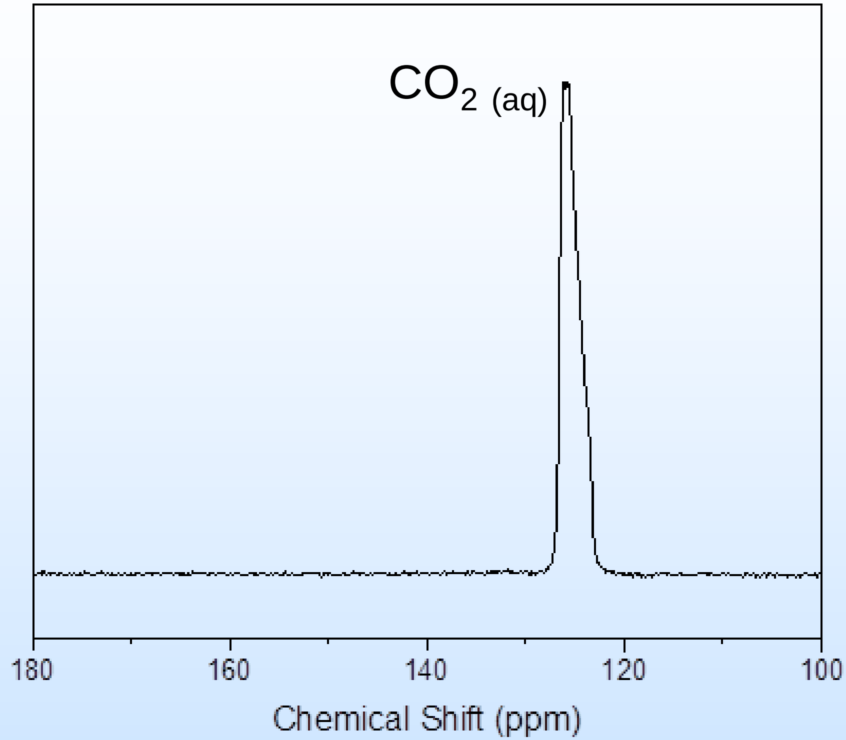
High Pressure NMR Hardware



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.

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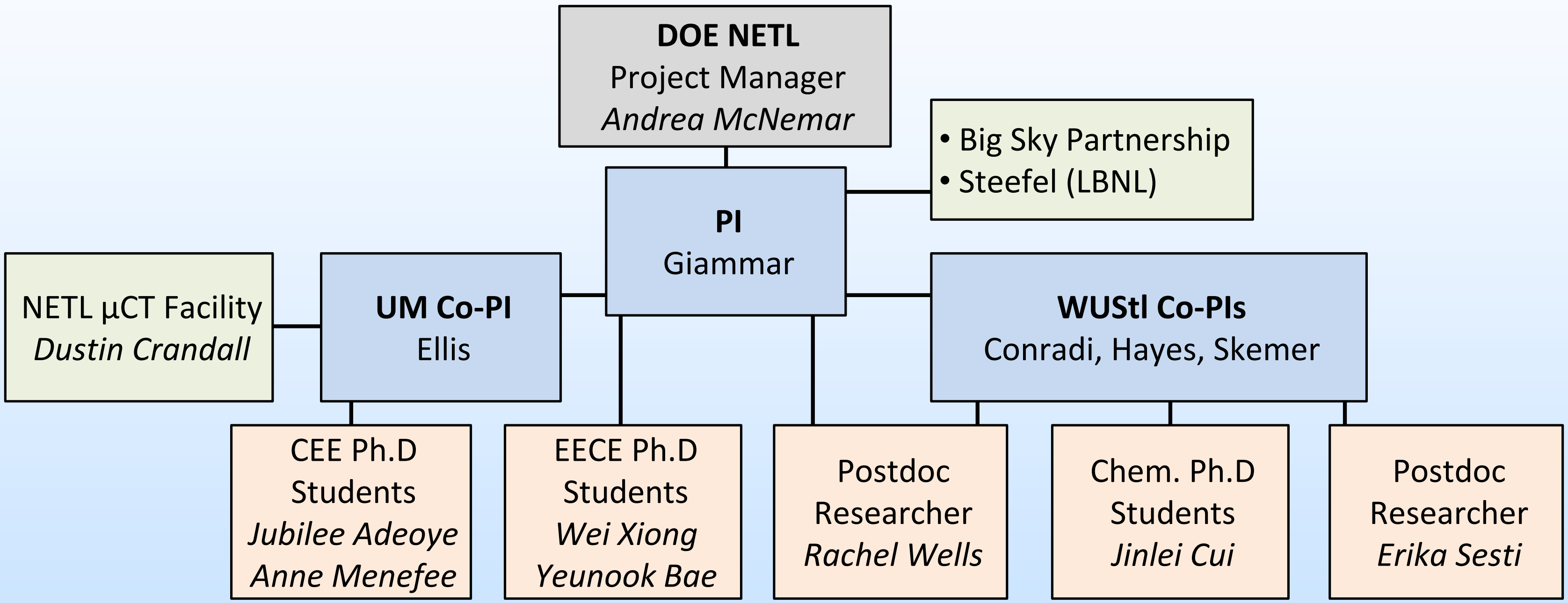
- Technical Support: Helene Couvy

Appendix

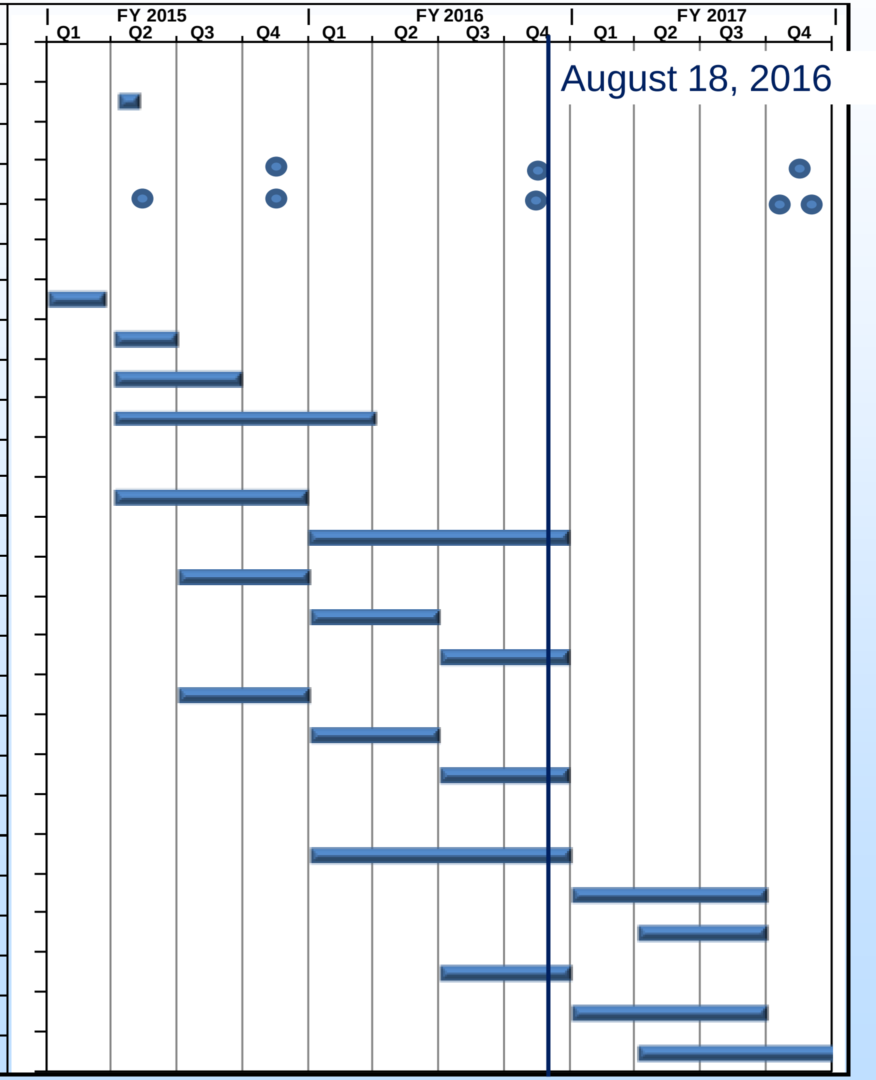
– Organization Chart
– Gantt Chart
– Bibliography

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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