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

Project Number DE-FE0023382

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- Technical Support: Helene Couvy

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Carbon Storage and Oil and Natural Gas Technologies Review Meeting
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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

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

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

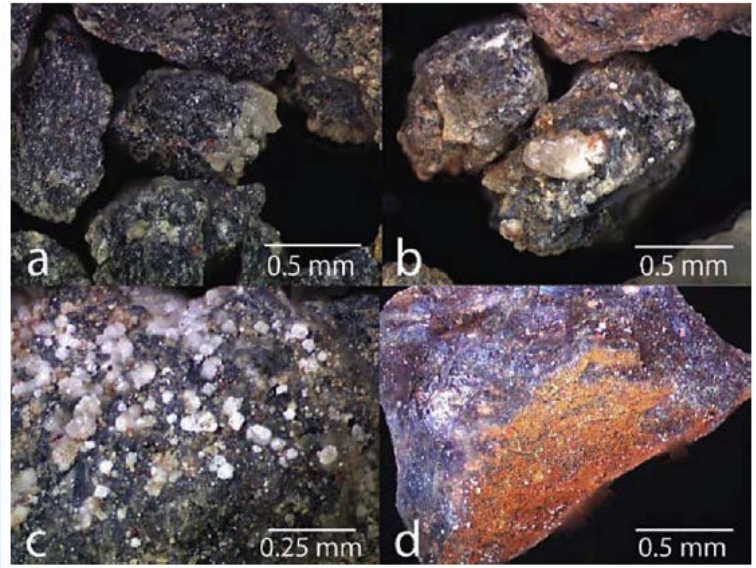
$$Fe_2SiO_{4(s)} + 4H^+ = 2Fe^{2+} + H_4SiO_4$$

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

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

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

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

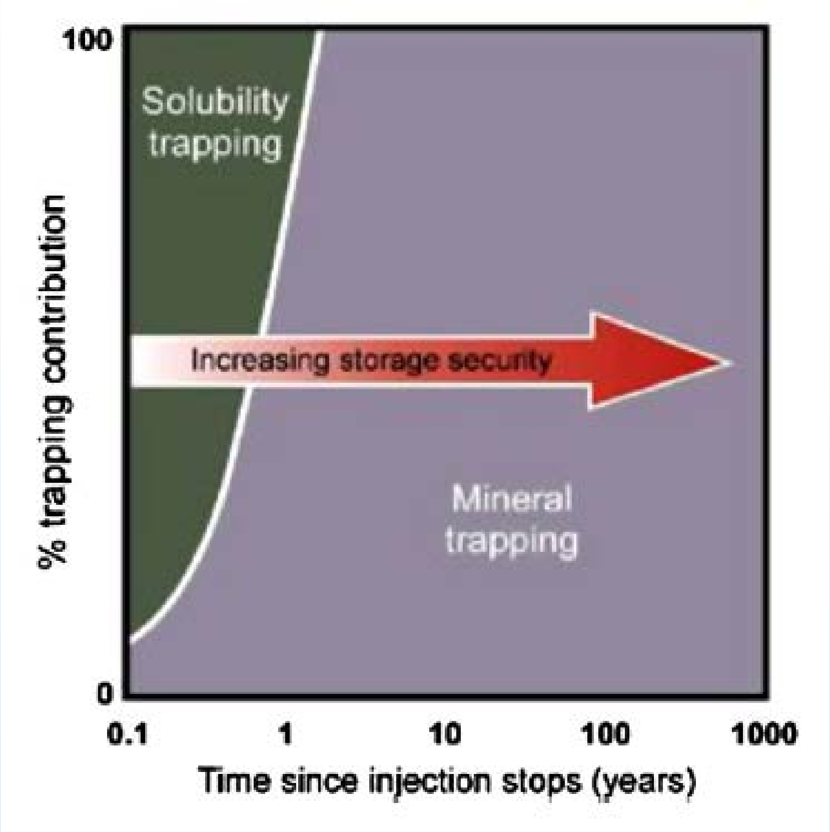


Carbonate precipitates on basalts after 854 days of reaction at 103 bar CO_2 and 100° C
Schaef et al., *Int. J. Greenhouse Gas Cont.*, 2010

- 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.

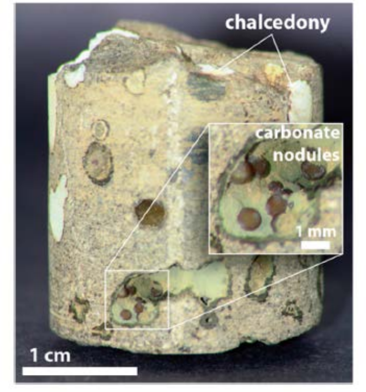
Pilot-Scale Injections into Basalts

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



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

Sidewall core from injection zone of Wallula, WA pilot well 24 months after injection of 1000 tons CO_2

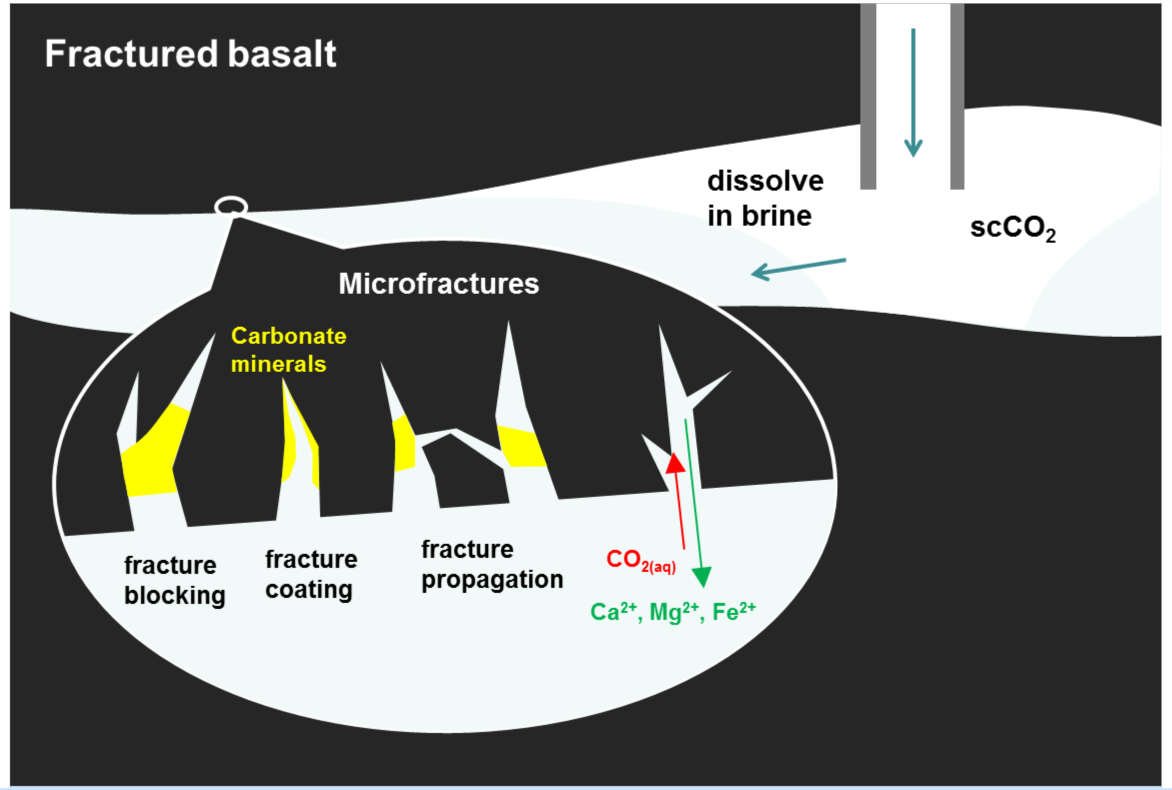


McGrail et al., *Environ. Sci. Technol. Lett,* 2017

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

Matter et al., *Science,* 2016

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

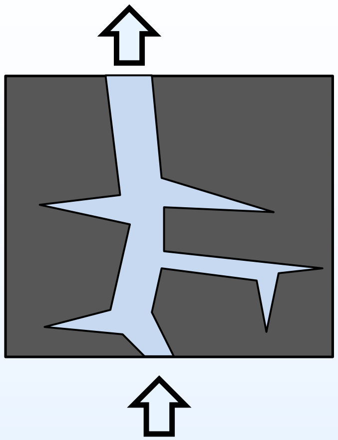
- Natural and artificial rocks
- Varying composition and fracture structure

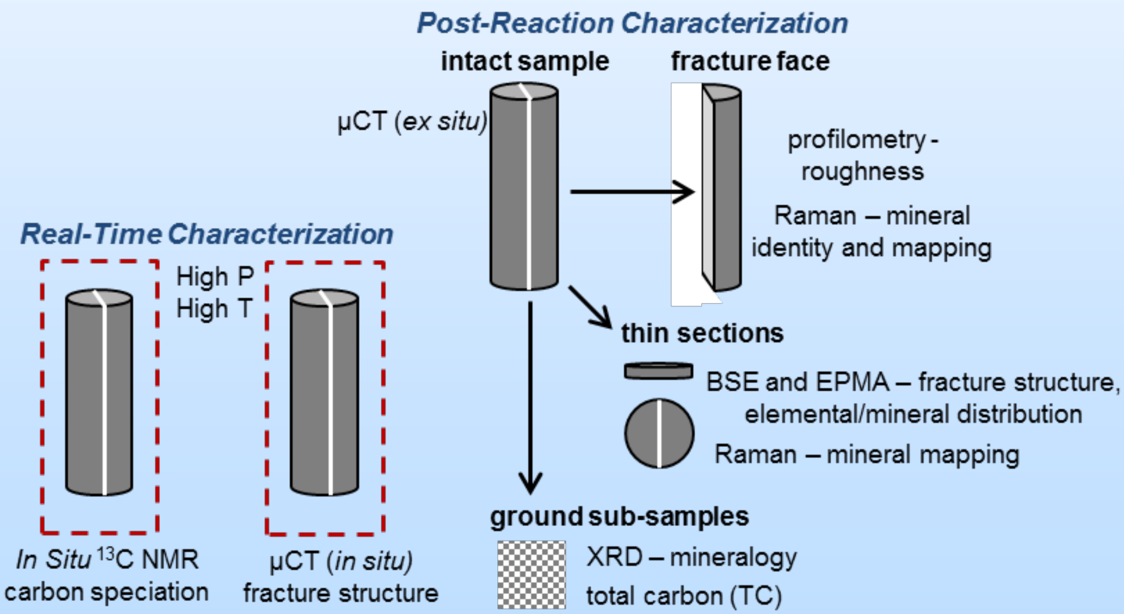
Bench-Scale Experiments

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

Characterization

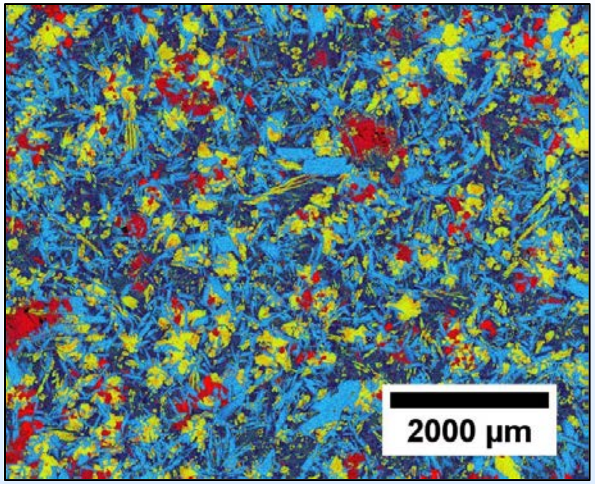
- Pre- and post-reaction
- *Ex situ* and *in situ* techniques.

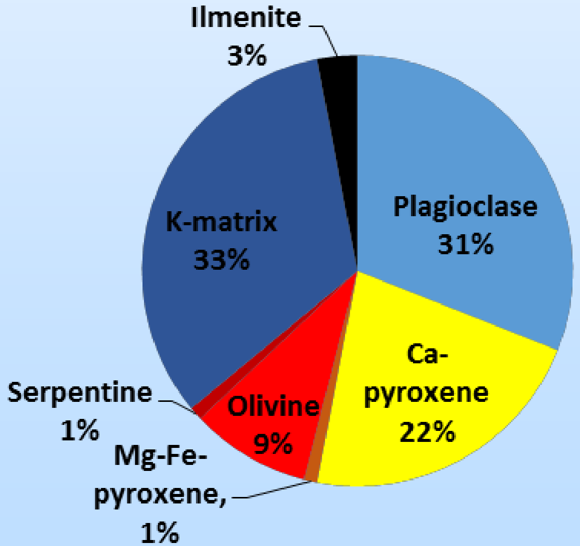




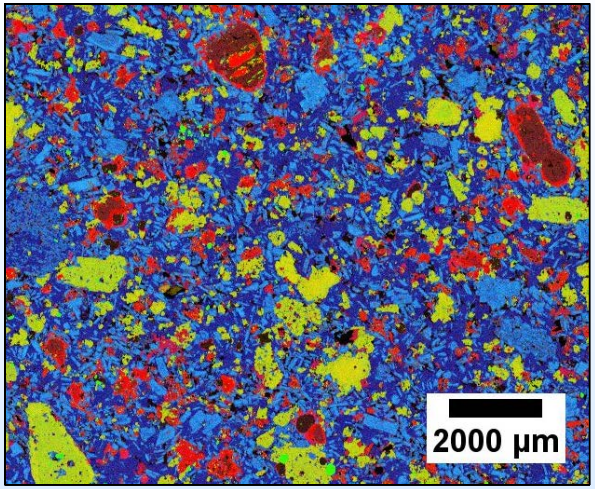
Basalt Materials

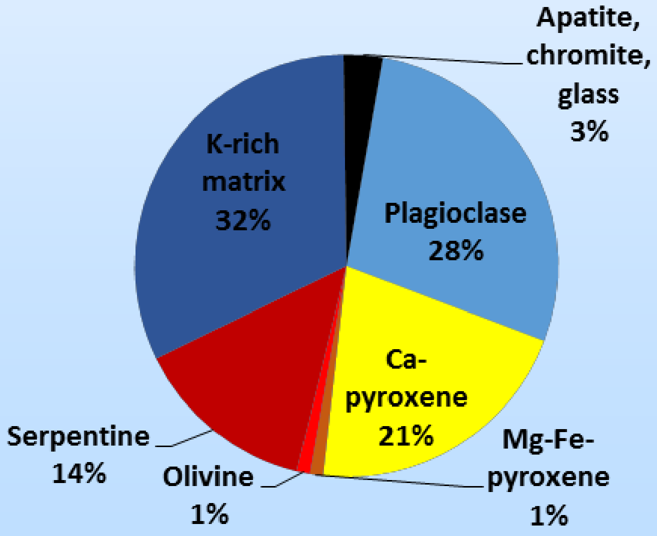
Columbia River flood basalt
(olivine rich)



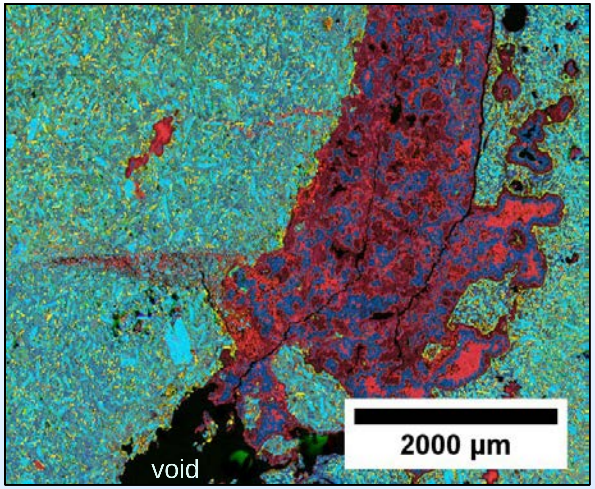


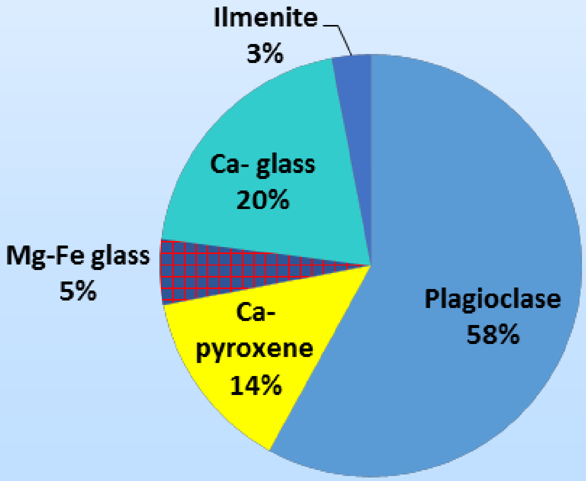
Colorado basalt
(serpentinized)





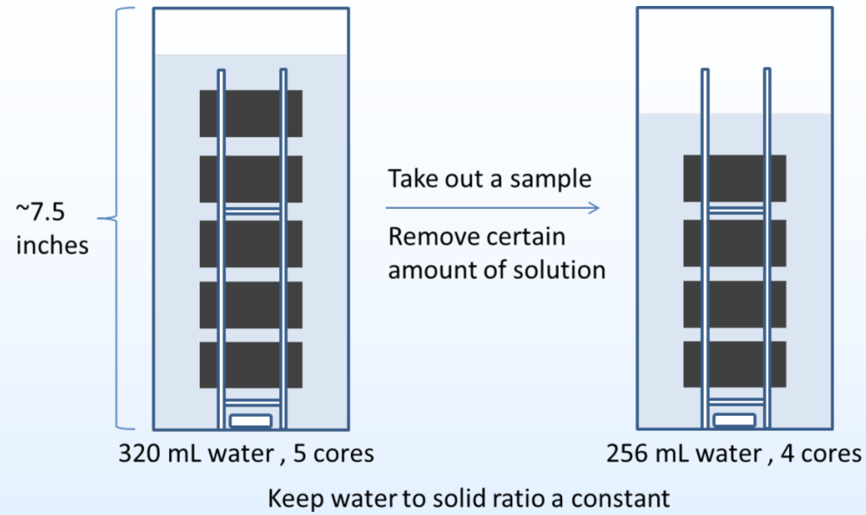
Grand Ronde basalt
(silica and calcium rich)

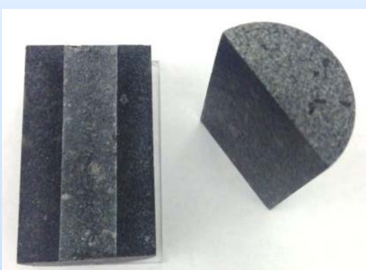




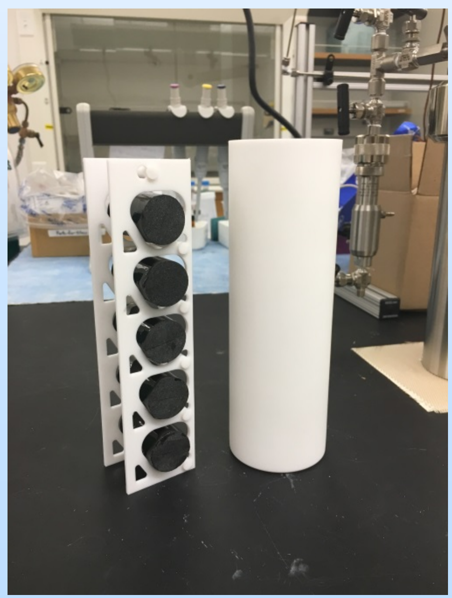
Basalt Core Experiments – Dead End Fractures

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



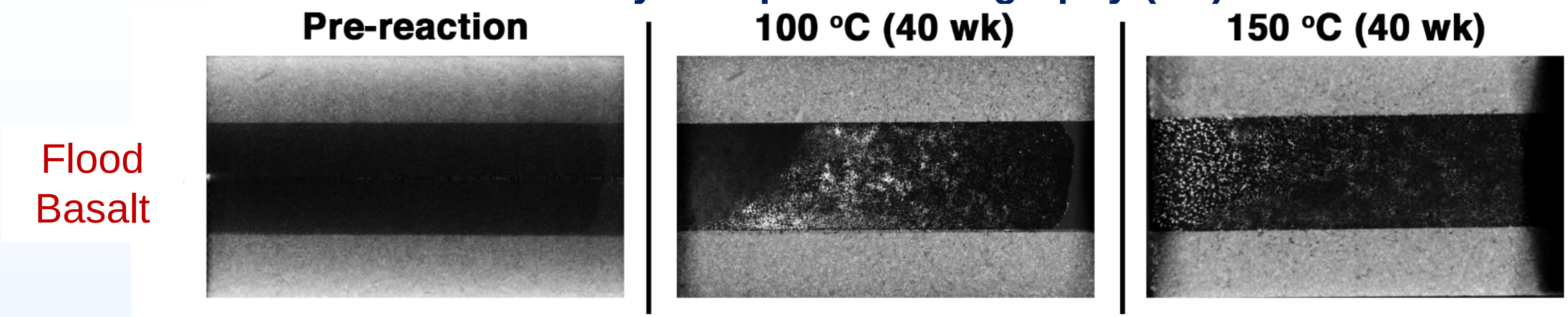


- Straight groove pattern
- ~11 mm wide
- 90-100 µm depth
- Coat with epoxy
- Expose the top surface

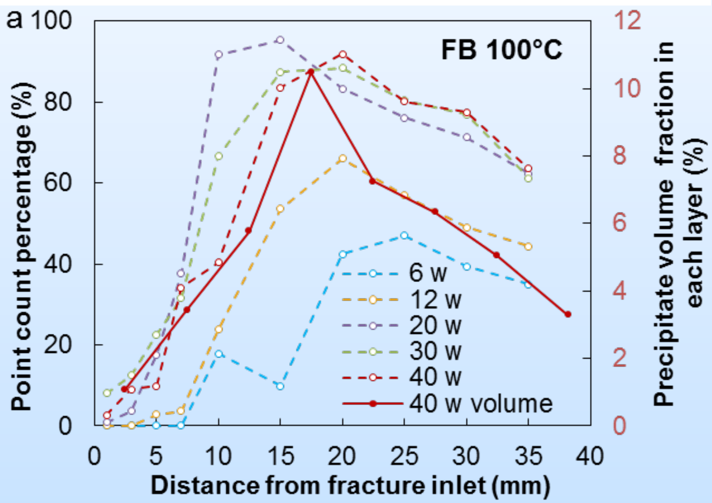


Carbonate Formation in Dead-End Fractures

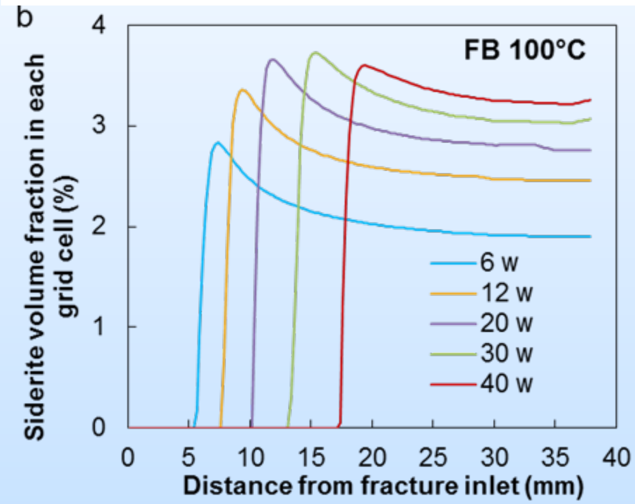
X-ray Computed Tomography (CT)



Optical Point-Counting

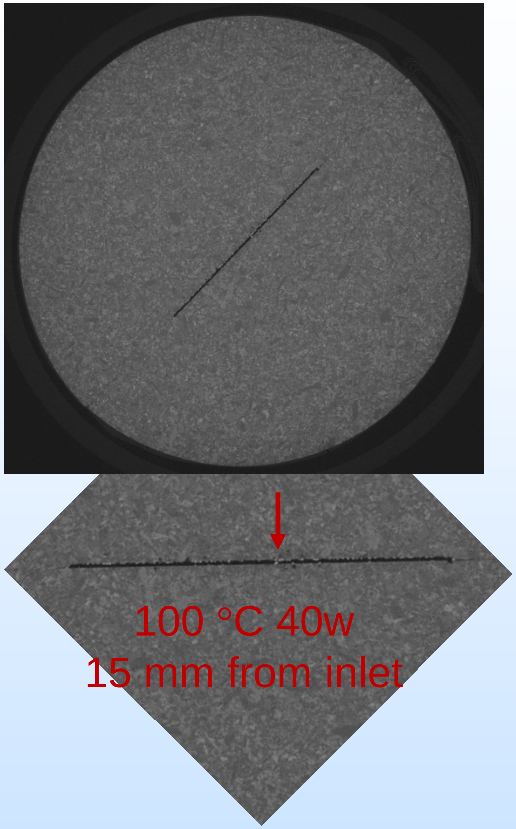


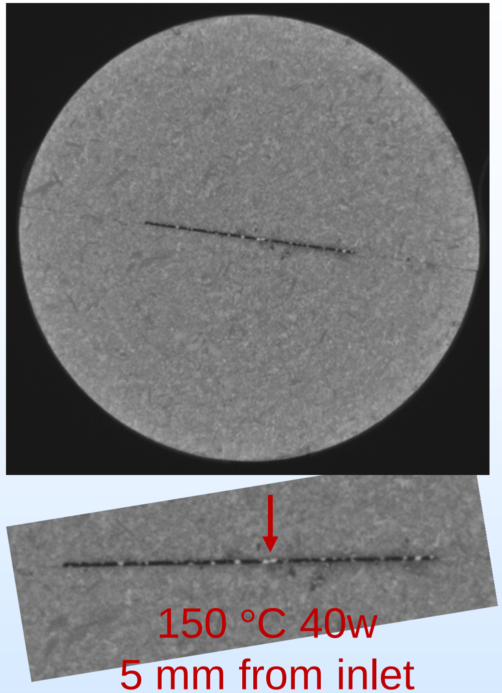
Reactive Transport Modeling

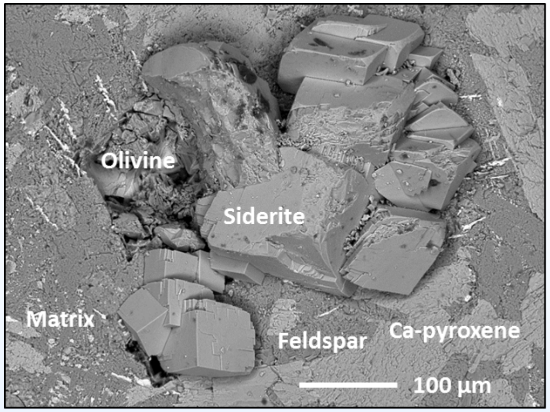


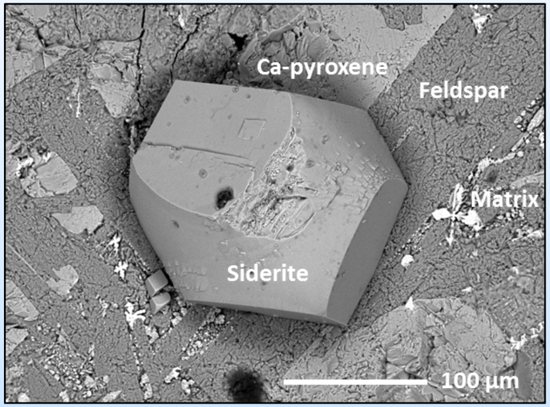
- Carbonate formation is spatially-localized.
- Reactive transport model output agrees with observations.
- Flood basalt is more reactive than serpentinized basalt (data not shown).

Carbonate Formation in Dead-End Fractures







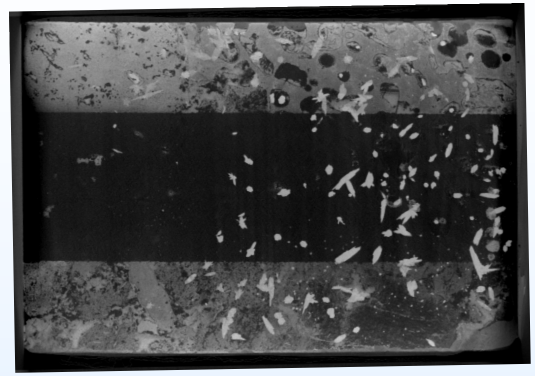


- Carbonates form as early as six weeks.
- Growth of carbonates does not completely seal the fracture by 40 weeks.
- Carbonates are siderite ($FeCO_3$) and a Ca-Mg-Fe carbonate solids
- Precipitates are large enough to bridge the 100 µm fracture.

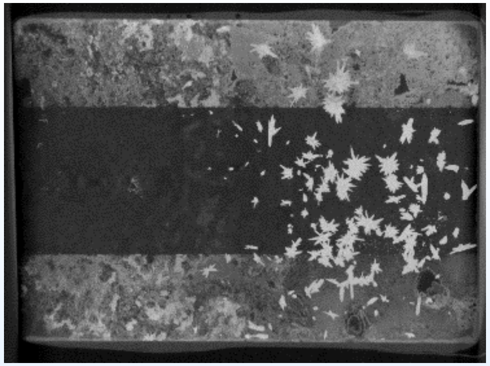
Grand Ronde Basalt (Relevant to Wallula)

Post-reaction: 6 weeks

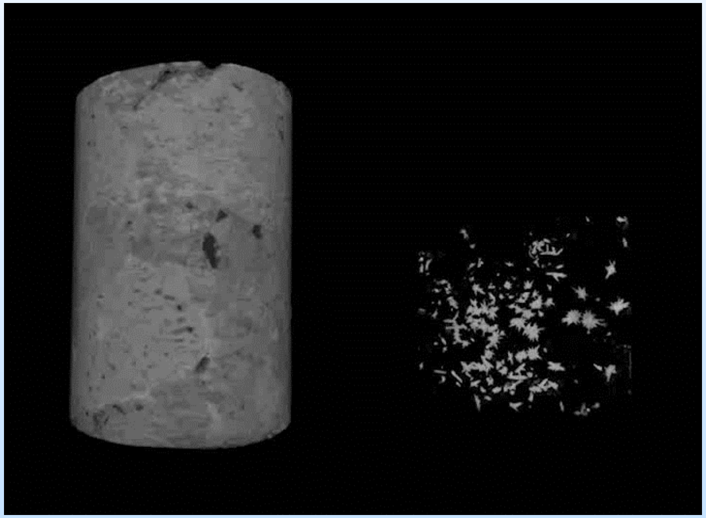
Post-reaction: 20 weeks

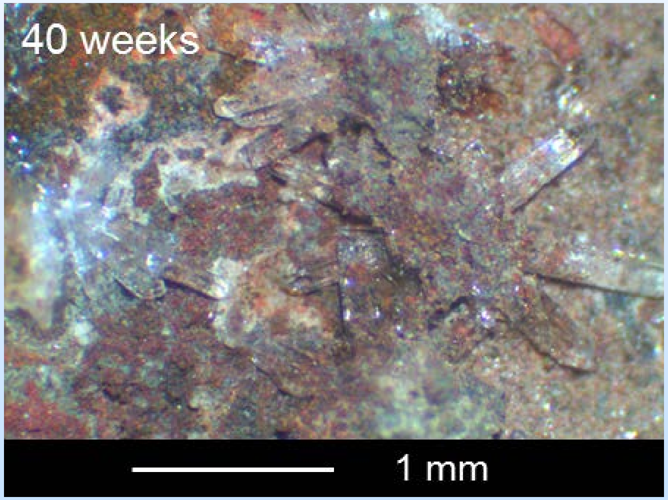


Post-reaction: 40 weeks



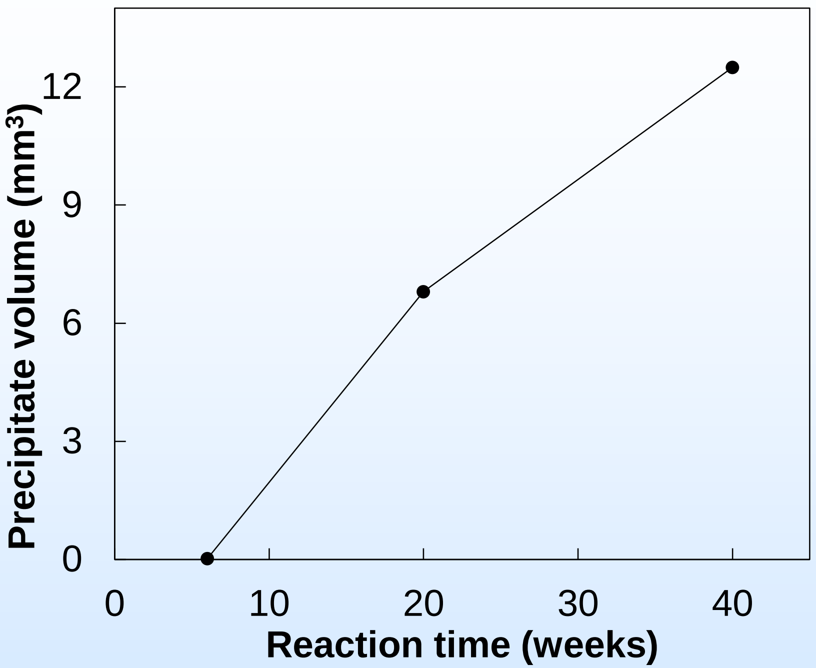
- cores in water
- 100 ºC
- 100 bar CO_2
- 3.7% average porosity





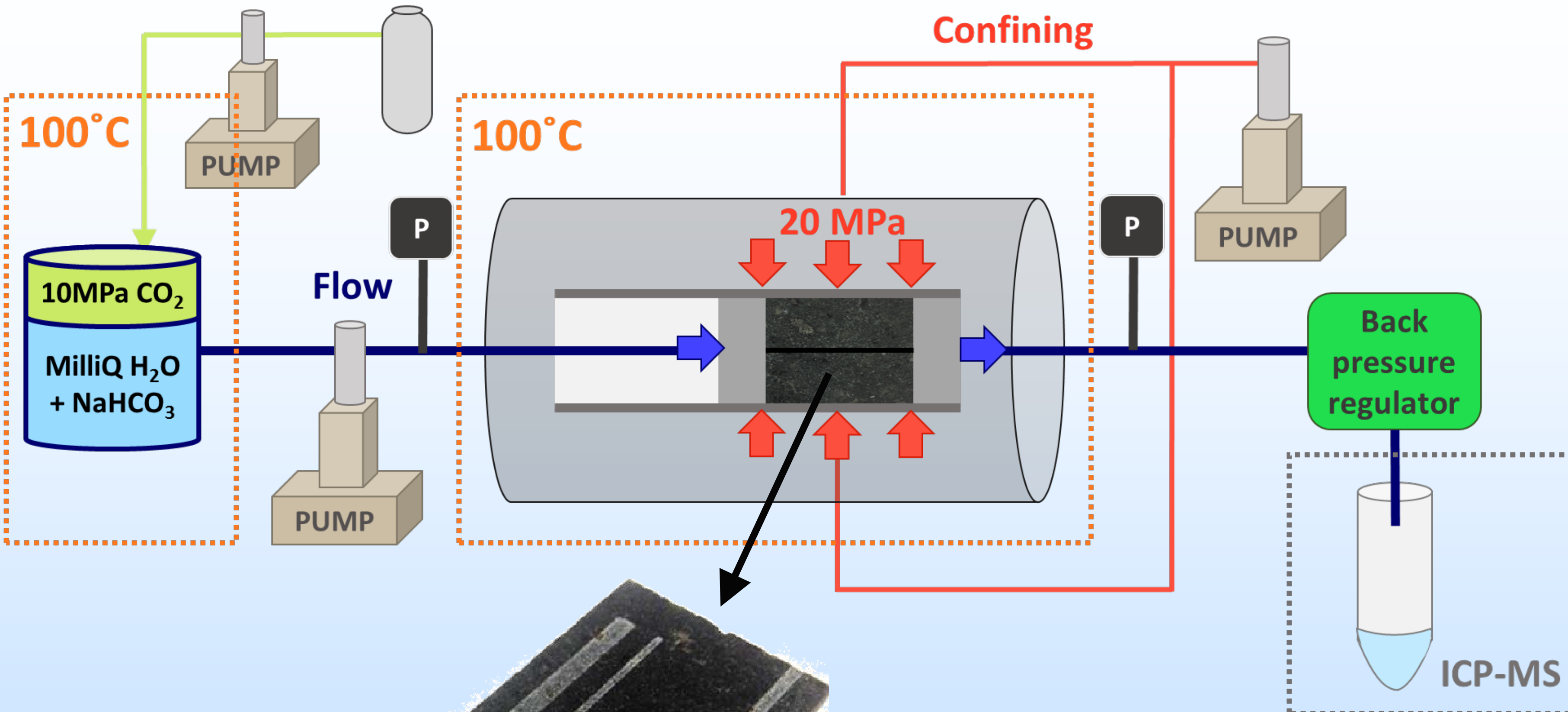
- Carbonates (predominantly aragonite) form as early as six weeks.
- Large precipitates form in milled fracture and in vesicles.

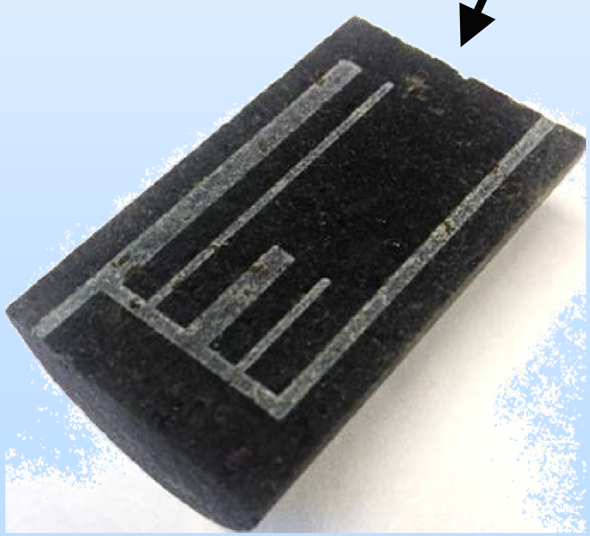
Carbon Trapping Rates and Capacity



- Carbonation rate = 1.24 ± 0.54 kg CO_2 / $m^3 \cdot y$
- Filling all porosity (3.7%) would trap **47 kg CO_2 / m^3**
- Could reach this capacity in **38 years**.
- Actual trend of mineral trapping with time is unknown.

Core Flooding Experiments

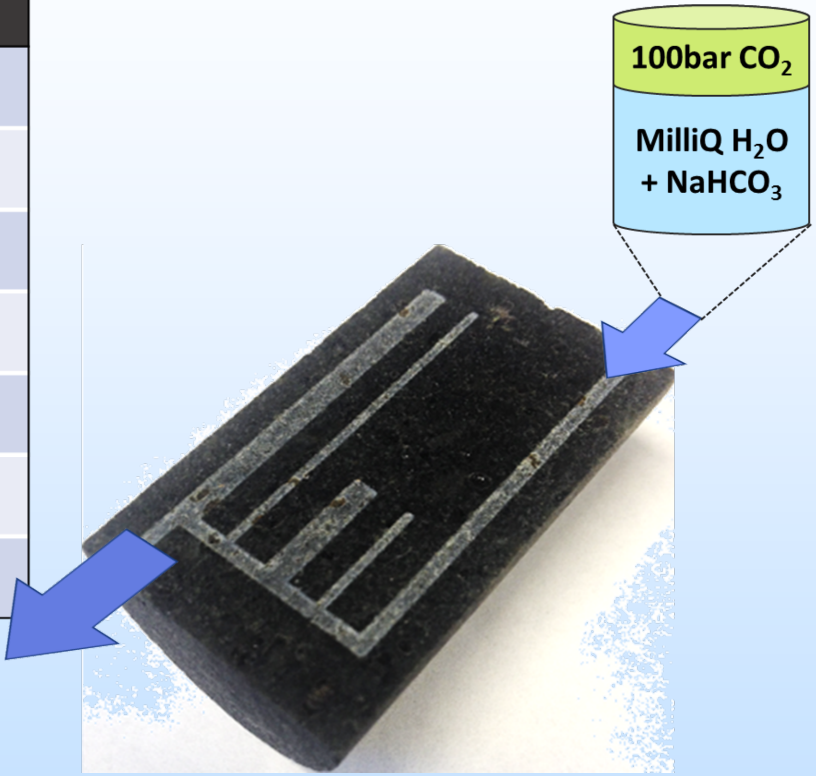




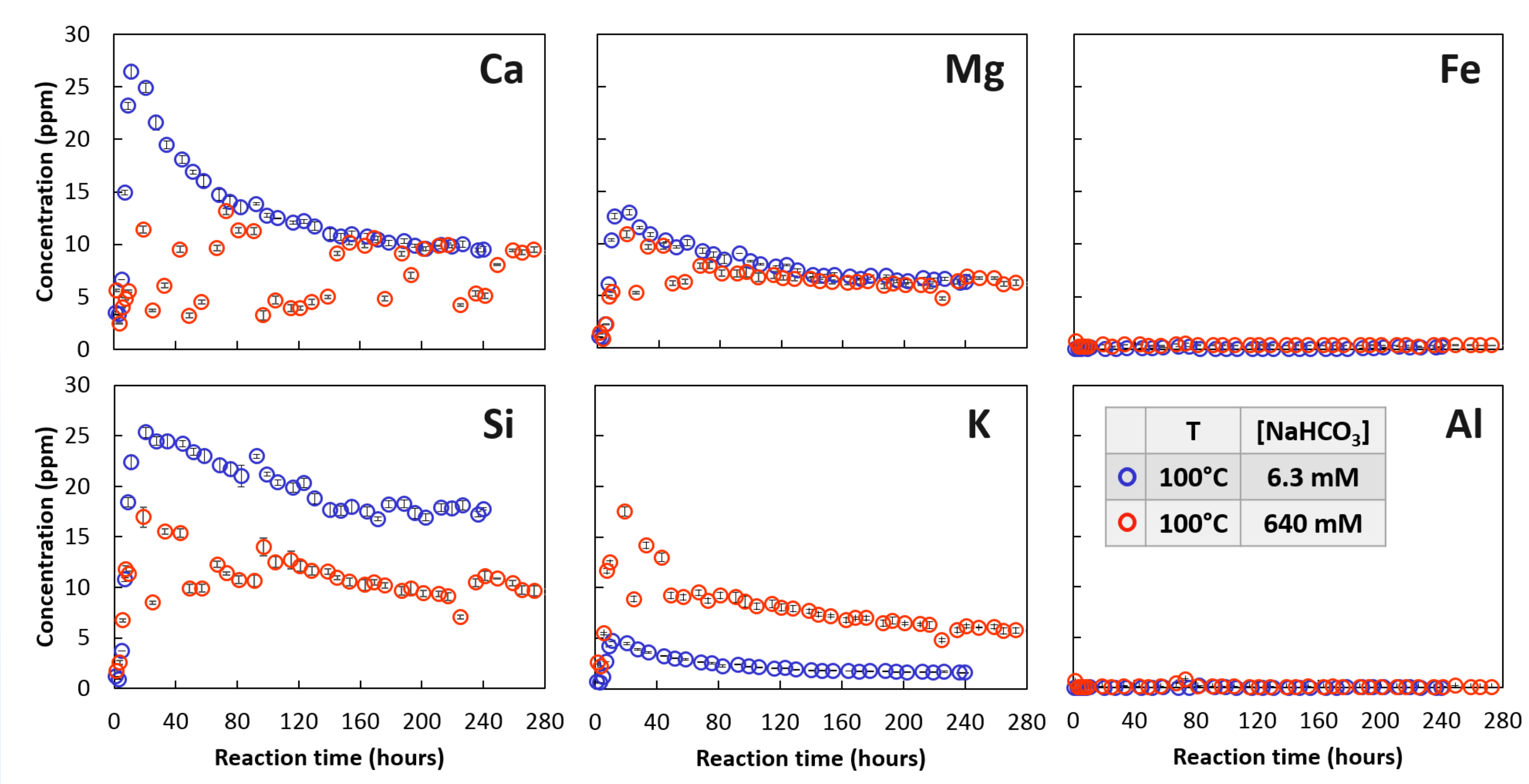
Optical microscopy
SEM/EDS
Raman spectroscopy
Pre-, post- CT scanning

Core Flooding Experiments

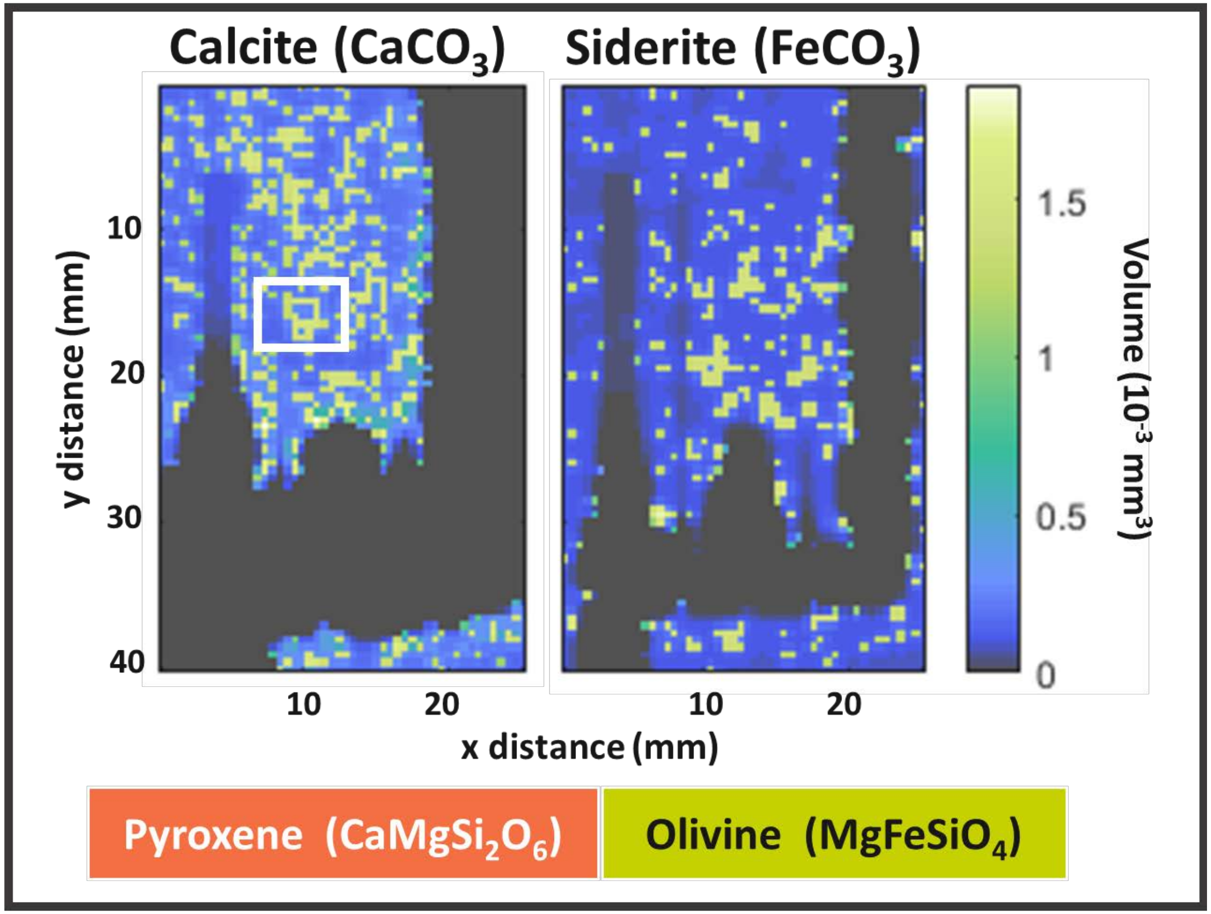
Condition	CB-1	CB-2
Temperature	100°C	100°C
P_{CO2}	20 MPa	20 MPa
Confining P	10 MPa	10 MPa
Flow rate	1 mL/hr	1 mL/hr
Initial [$NaHCO_3$]	**6.3 mM**	**640 mM**
Initial pH	4.2	6.0
Duration	10 days	12 days

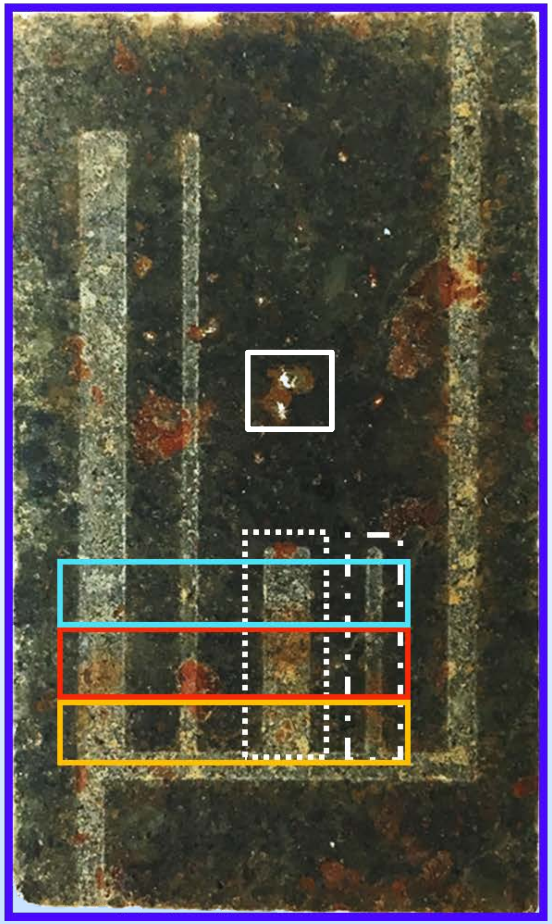


Effluents from Core Flooding Experiments



Geochemical Gradients





- Sample with 6.3 mM $NaHCO_3$ 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.

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- 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.

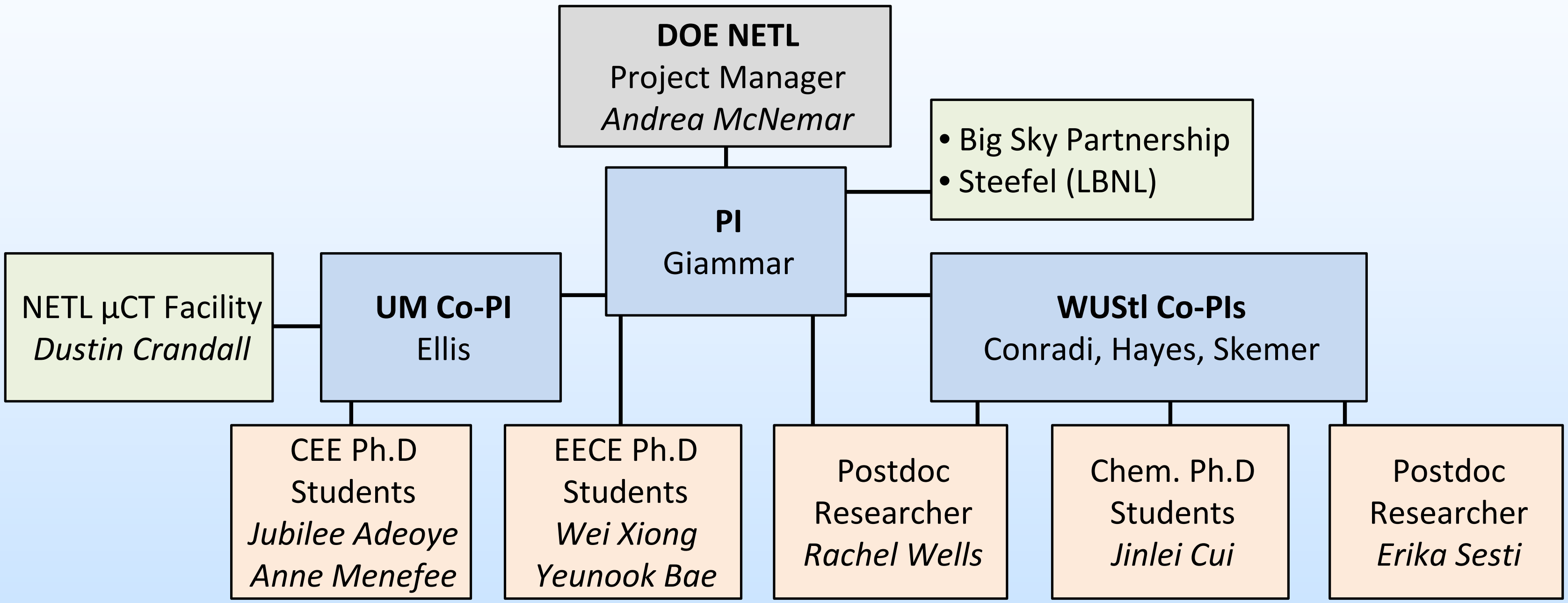
Project Overview:
Goals and Objectives

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.

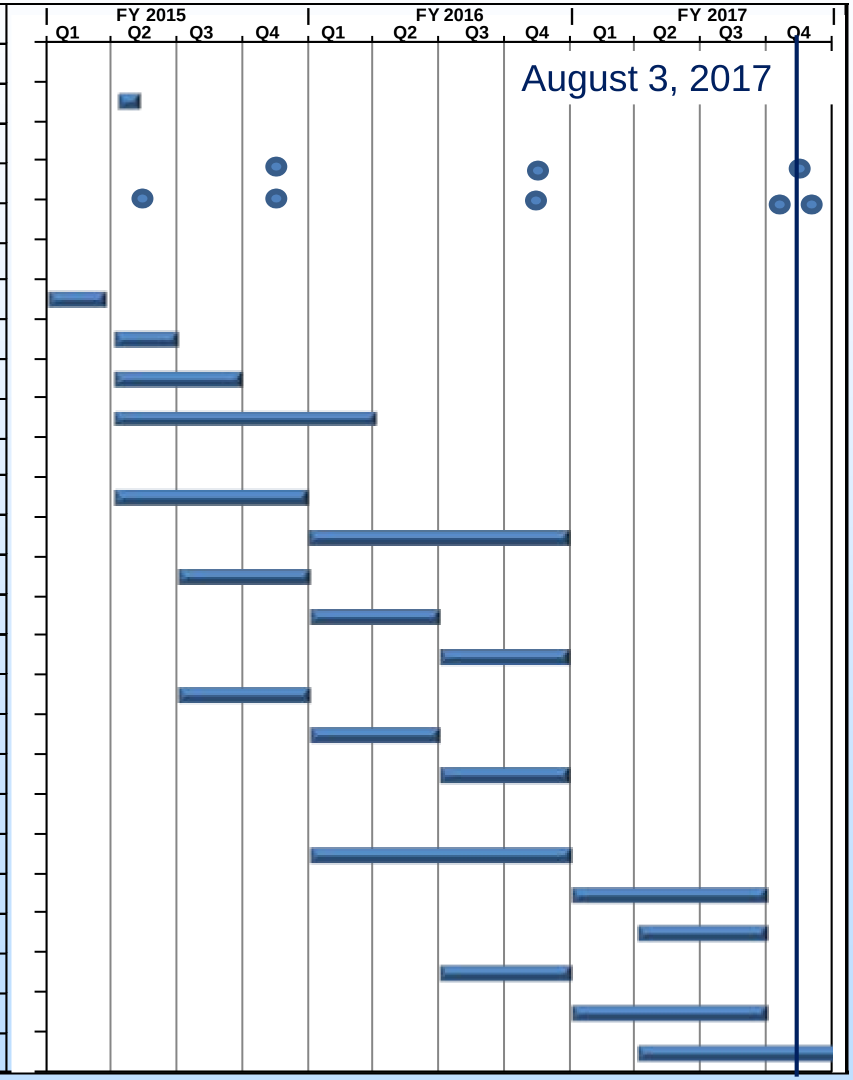
Organization Chart



Gantt Chart

Received no-cost extension through March 31, 2018

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



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