# Sequestration in Basalt Formations

FWP-73235

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 28 – September 1, 2023
Carbon Transport and Storage Breakout Session 2
Tuesday 1:10pm, 315/316

H. Todd Schaef

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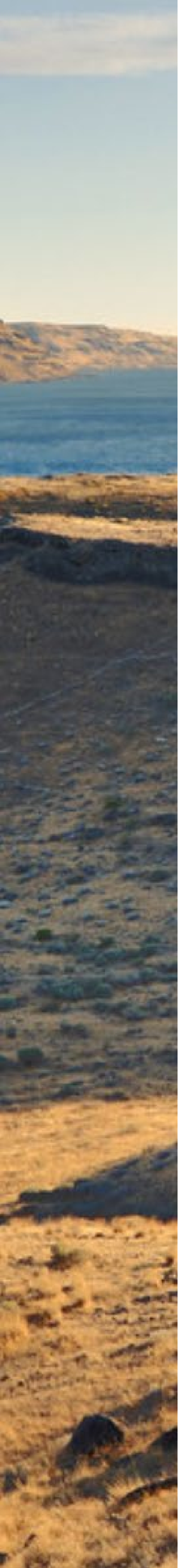
Photo: Andrea Starr (PNNL

# Presentation Outline

- Project Overview
  - Key Project participants, Project objectives, Project performance dates, Funding summary
- Project Background
  - Brief Project history, Project location(s), Importance of project towards advancing DOE Program Goals
- Technical Approach/Project Scope
  - High-level Project execution plan, Project schedule summary including key milestones, Project success criteria/ expected outcomes, Summary of high probability and/or high impact project risks, with mitigation strategies
- Current Status of Project and Accomplishments (*Focus of the presentation*)
  - Status of project objectives and tasks, Summary of significant accomplishments / key findings and their impact, Summary of significant challenges and mitigations
- Summary of Community Benefits / Societal Considerations (CB/SCI) and Impacts
  - Summarize CB/SCI efforts planned or undertaken as part of the project, Summarize progress towards CB/SCI SMART milestones
- Next Steps
  - For Project, After Project/ Scale-up potential
- Summary of Lessons Learned to date



# Health, Safety, and Environment Share: Everyday Respect


- Leaders need to be the shining examples of everyday respect
- Caring, courageous and curious leadership
- Elevate process over results
- Cultivating talent, not teams

**5 Ways To Promote Respect In The Workplace**

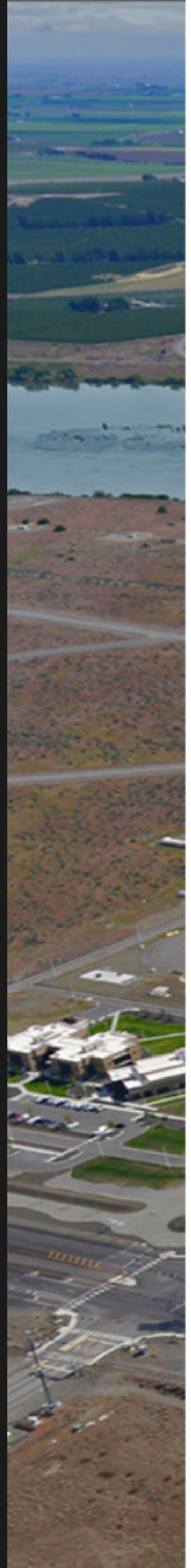
- Choose Your Words Carefully
- Make Soft Skills a Priority
- Resist All Forms of Exclusion
- Clearly Articulate Zero Tolerance for Harassment
- Get Transparent

# Project Overview

- Key Project Participants
  - State/Federal, National Lab, Universities, and Industry

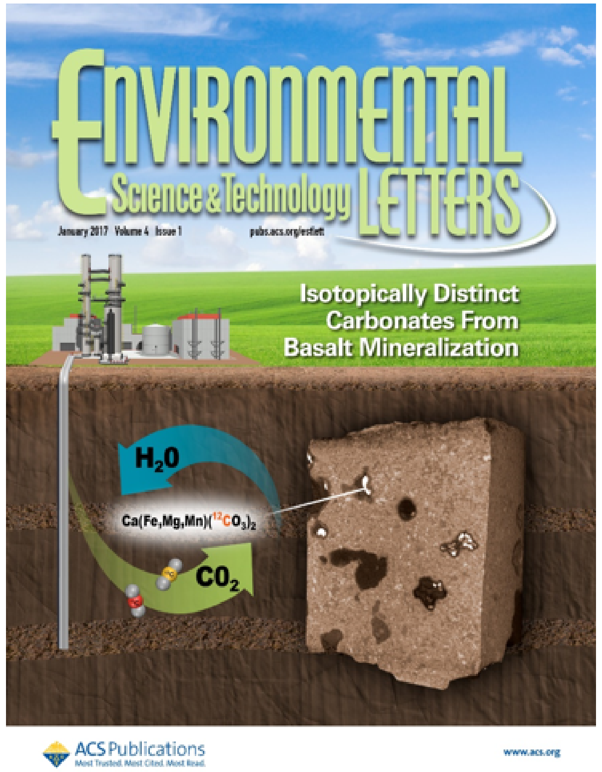
## Collaboration Development

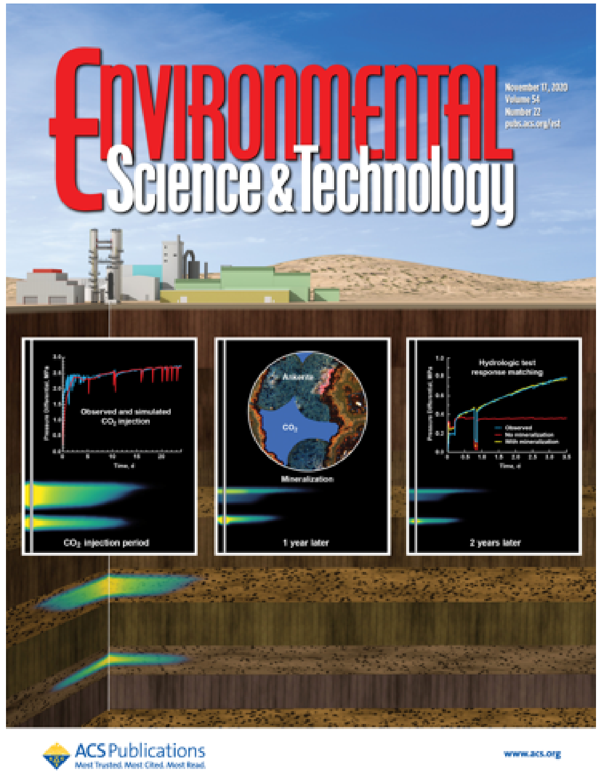
state/federal national labs universities industry



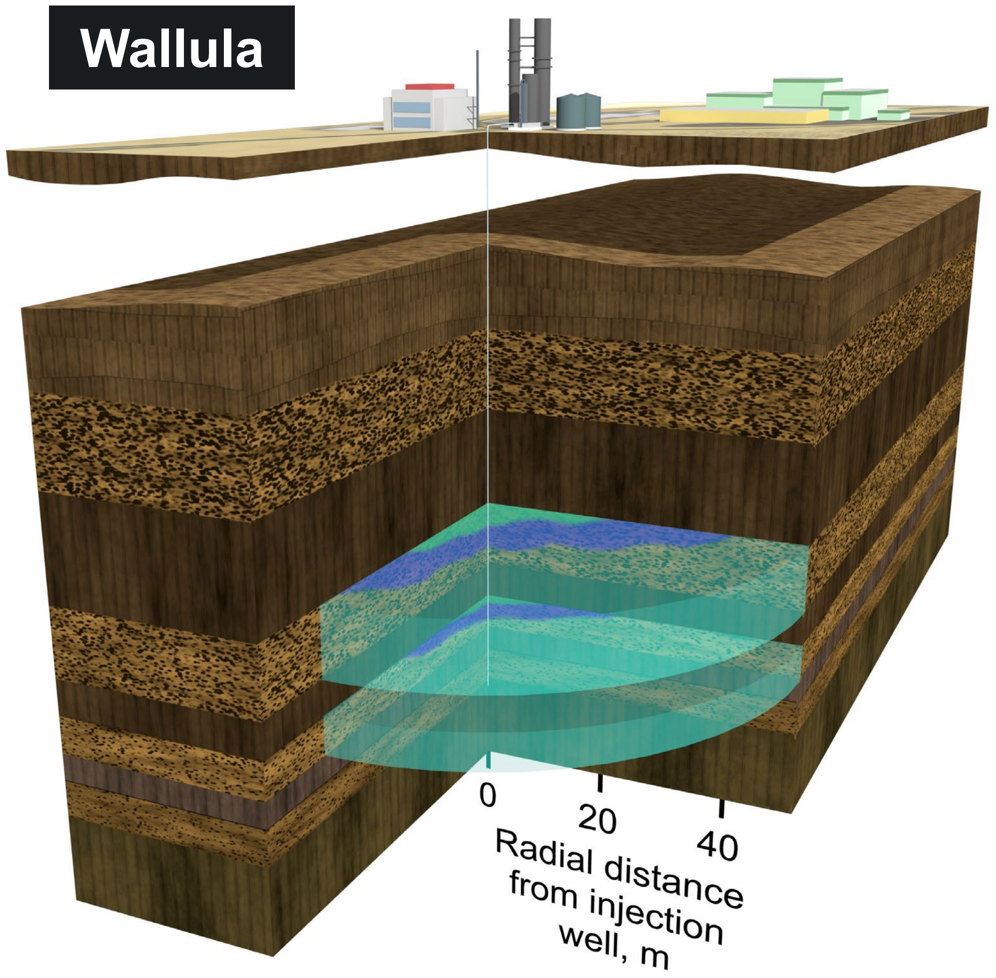
# Project Overview

- Key Project Participants
  - State/Federal, National Lab, Universities, and Industry
- Project Objectives
  - Provide support for post-closure characterization activities associated with the Wallula Basalt Pilot Well.
  - Biomineralization reactions affecting the effectiveness of $CO_2$ injection, stability of primary minerals in the reservoir and caprock, precipitation of secondary carbonate minerals, and potential impacts to associated critical minerals (e.g., release rates, precipitation products, etc.)
  - Create and disseminate reactive modeling tools that can simulate interactions of $scCO_2$ fluids in basaltic reservoirs.
- Project Performance Dates and Funding Summary
  - FY21 \$200K; FY22 \$150K; FY23 \$250K



# Project Background

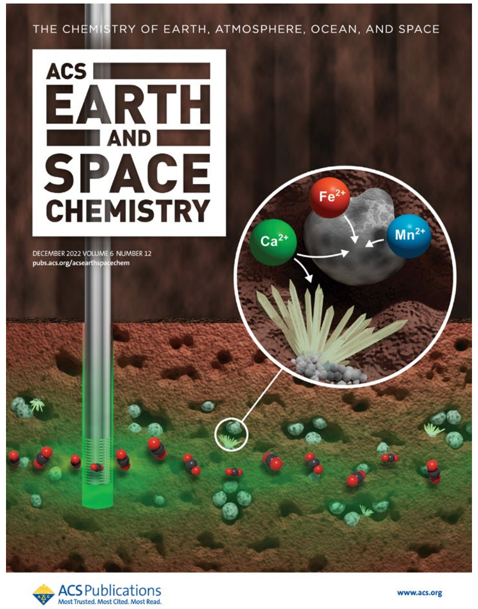



**MINERALIZATION SETTINGS**

- Targets for in situ $CO_2$ mineralization include:
  - Porous reservoirs (e.g., basalts)
  - Fractured reservoirs (e.g., peridotite, serpentinite)
  - Hybrid systems (e.g., fractured basalt-hosted geothermal reservoirs, basalt-rich sandstones)
- Ex situ mineralization efforts focus on mine tailings, soil amendments, and engineered systems that leverage non-ambient conditions

**BASALT GEOCHEMISTRY**

- Basalts are comprised of crystalline minerals (feldspars, pyroxenes, olivine) within a highly reactive glassy matrix
  - carbonate-forming cations (e.g., $Ca^{+2}$, $Fe^{+2}$, $Mg^{+2}$, and $Mn^{+2}$)
- Carbonate type controlled by depth, temperature, surface area, pre-existing secondary minerals, pressure, & water chemistry




**Opportunities to Solve Challenges:**

- Assessing mineral carbonation processes from the SWCs retrieved post $CO_2$ injection, providing a unique perspective on subsurface carbon mineralization.
- Develop modeling tools that incorporate critical insights from field and laboratory studies to advance $CO_2$ mineralization storage

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# Technical Approach/Project Scope For FY22 & FY23 (by task)

## FY22 (FY23-24) Scope

**Task 1**: Post-closure characterization activities associated with the Wallula Basalt Carbon Sequestration Pilot Well

## FY23 Scope

**Task 1:** Biomineralization Literature Review

- Review biomineralization in ultra mafic and mafic rocks and minerals, guiding Task 3, 4

**Task 2:** Biosignatures of Natural and Anthropogenic Wallula Carbonates

- Evaluate role of biogenic carbon cycles on carbon mineralization at the Wallula site

**Task 3:** Biomolecule Enhancement of Carbonation

- Explore role of biomolecule proxies on carbonate precipitation in mafic and ultramafic rocks and minerals.

**Task 4:** CM Outcomes During Carbonation

- Fate of CM in the presence of biomineralization

**Key Objectives:**

- Extracting key information from the post-injection/pre-closure phase of the basalt pilot project, with a focus on assessing mineral carbonation processes from the SWCs retrieved post $CO_2$ injection.
- Enhancing carbonation of basalt through biomineralization and determining the fate of critical minerals in these formations.
- Provide to the mineralization community key data to advance $CO_2$ mineralization in reactive reservoirs.
- Support and advance MRV for mineralization.

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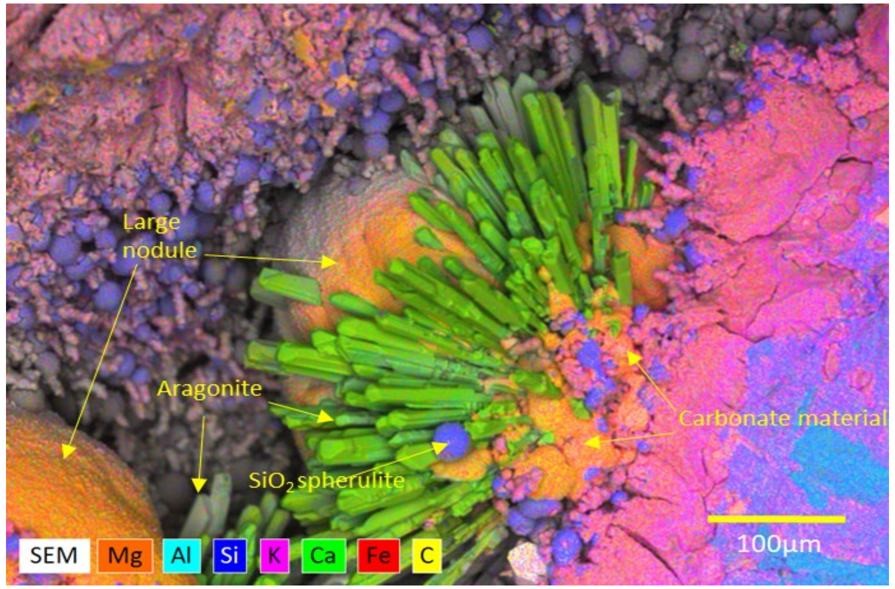
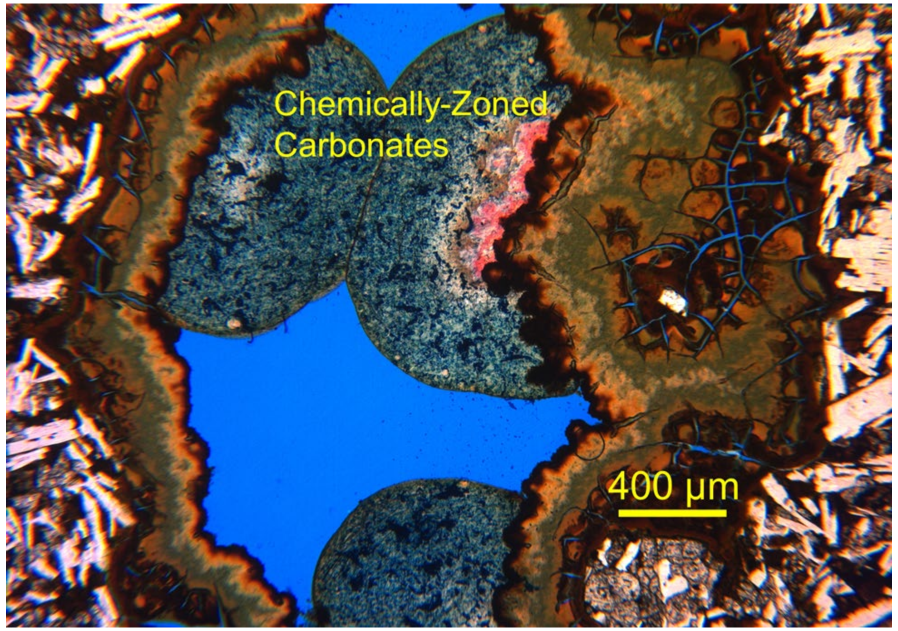
# Predicting $CO_2$ Mineralization Requires Understanding Reaction Pathway Endpoints

## $CO_2$ mineralization processes are overlapping and complex

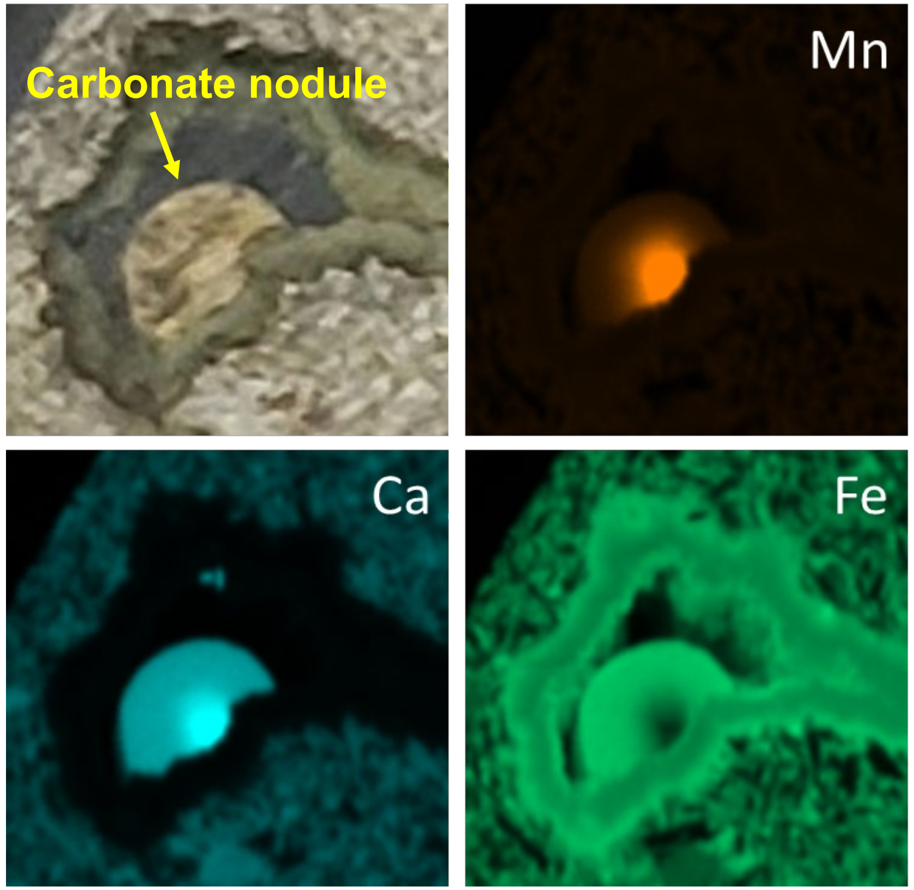
- Observed carbon mineralization assemblages at Wallula include aragonite ($CaCO_3$), siderite ($FeCO_3$), ankerite [$Ca(Fe,Mn)(CO_3)_2$], and non-carbonate minerals
- Chemically-zoned carbonate nodules (Ca, Mn, and Fe)
- Unique chemistries directly correlated to pre-existing pore-lining minerals.




Depp et al., 2022, Pore-scale Microenvironments Control Anthropogenic Carbon Mineralization Outcomes in Basalt, ACS Earth Space Chem




Polites et al. 2022, Exotic Carbonate Mineralization Recovered from a Deep Basalt Carbon Storage Demonstration, ES&T



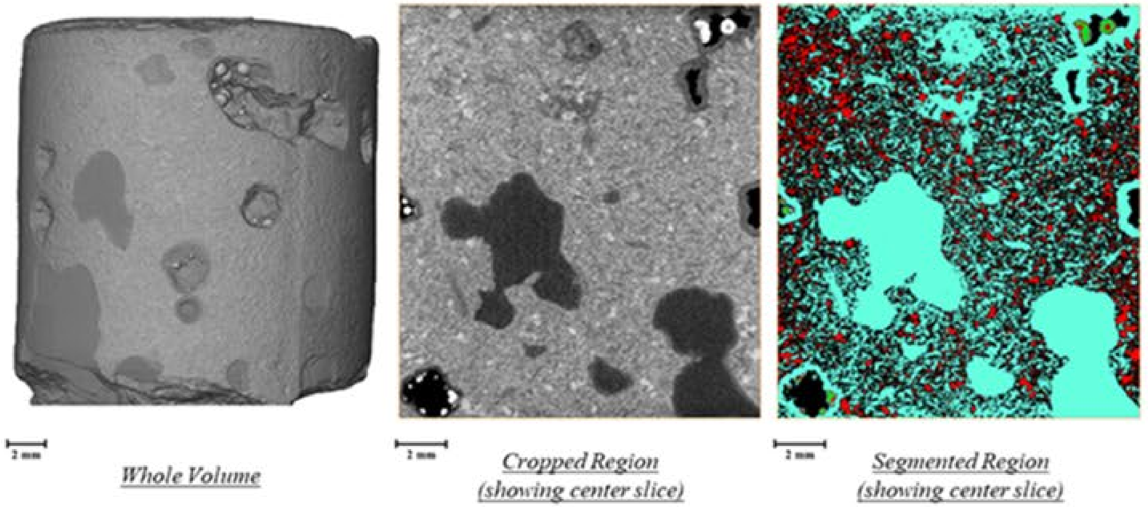

Lahiri et al., 2023, Facile Metal Release from Pore-lining Phases Enables Unique Carbonate Zonation in a Basalt Carbon Mineralization Demonstration, ES&T

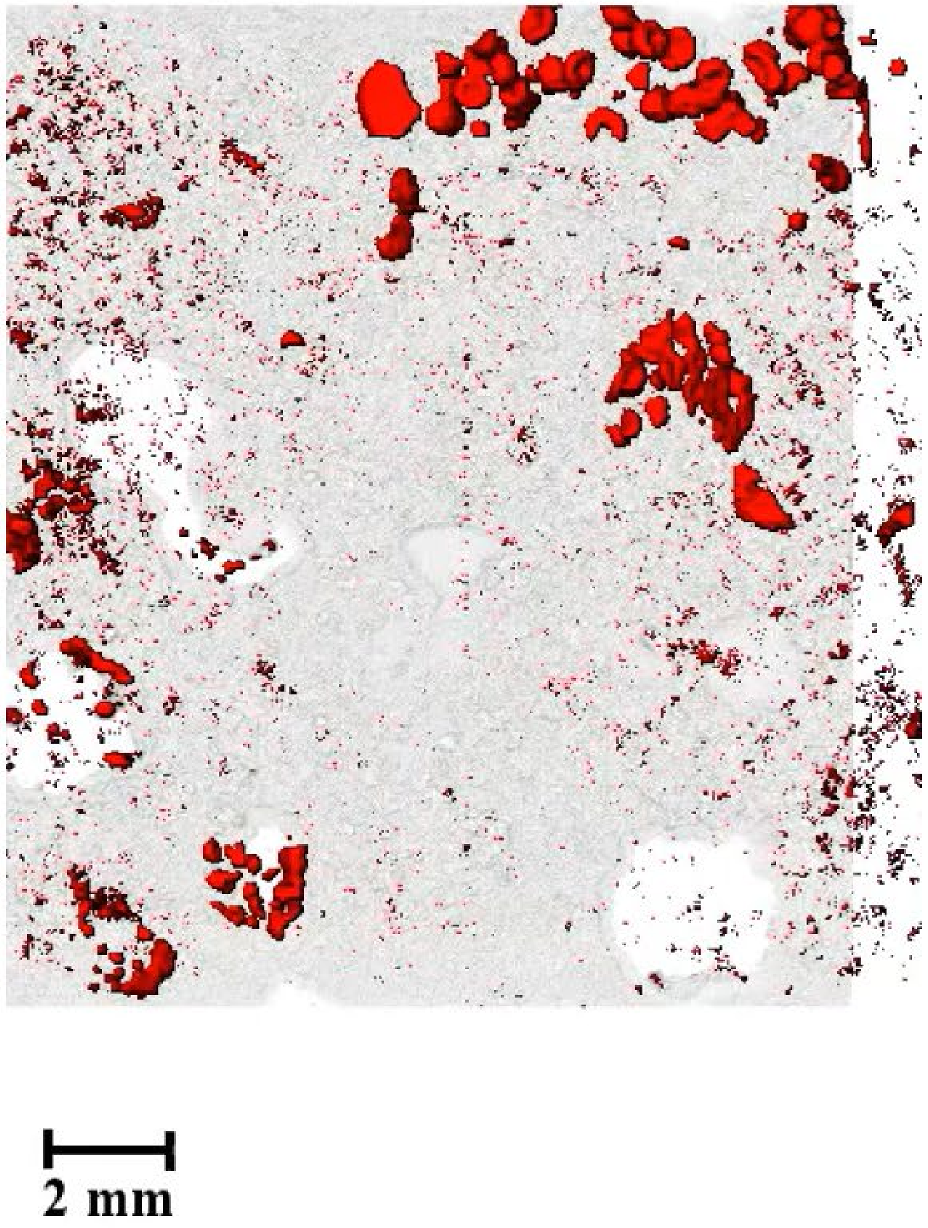
**Key Questions and Knowledge Gaps:**

- What types of realistic parameters and sensitivity analysis are needed to establish mineral transformation rates?
- Robust characterization criteria/methodologies for pre-and post-$CO_2$ injection are needed
- Existing databases do not contain new exotic carbonate mineral compositions and structures observed at Wallula
- **How can we establish a predictive understanding of complex carbon mineralization outcomes in subsurface conditions?**

# Quantification of Basalt Pore Network Architecture and Carbon Mineralization Extent

- X-ray microtomography allows for pore network quantification and determination of phase abundances and spatial associations
- XMT captures internal zonation of carbonate nodules
- Information is being used to parametrize reservoir models (e.g. reactive surface area) and quantify degree of carbon mineralization at Wallula



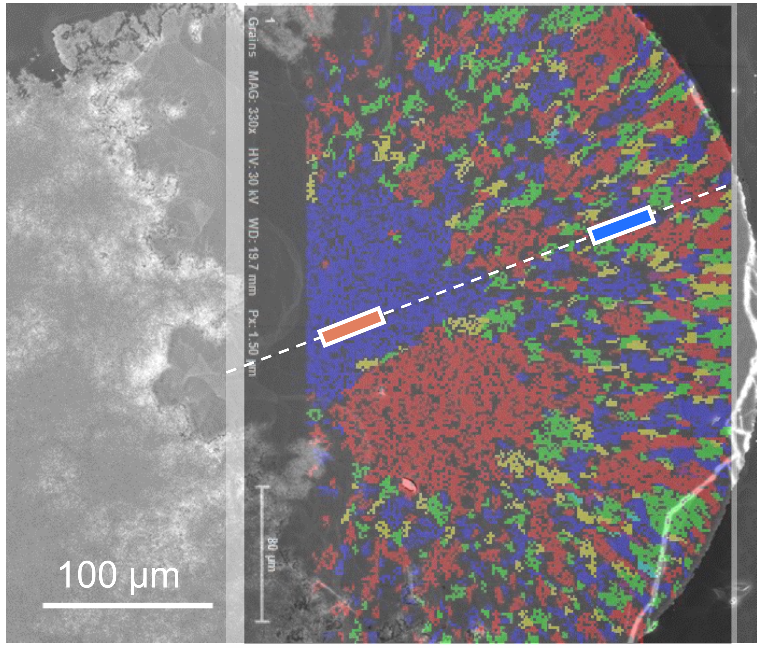




**Key Outcomes:**
- Quantify impacts to porosity (pre and post $CO_2$ injection)
- Carbonate morphology, carbonation quantification (post injection)

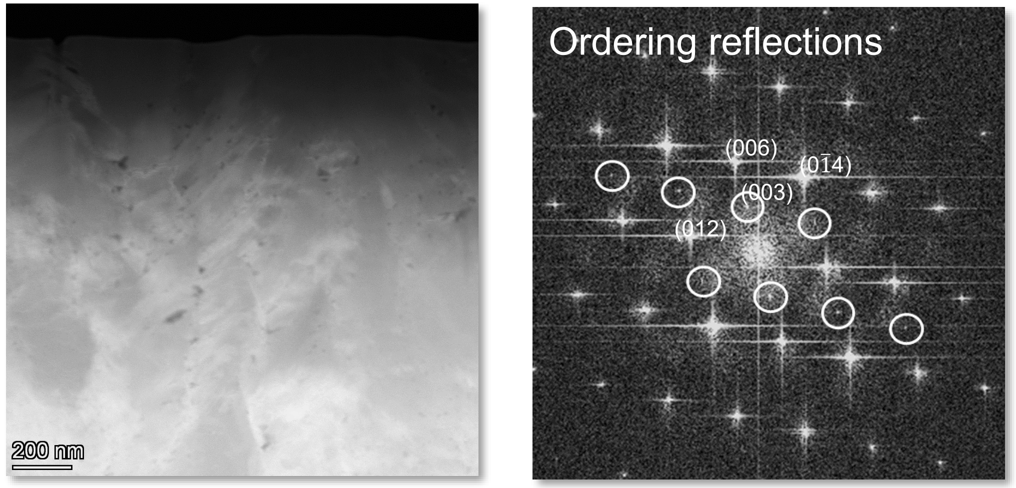
Battu et. al., 2023. 3D Quantification of Pore Networks and Anthropogenic Carbon Mineralization in Stacked Basalt Reservoirs, ES&T, submitted.

# Nanoscale Insights Enable Refinement of Predictive Geochemical Modeling

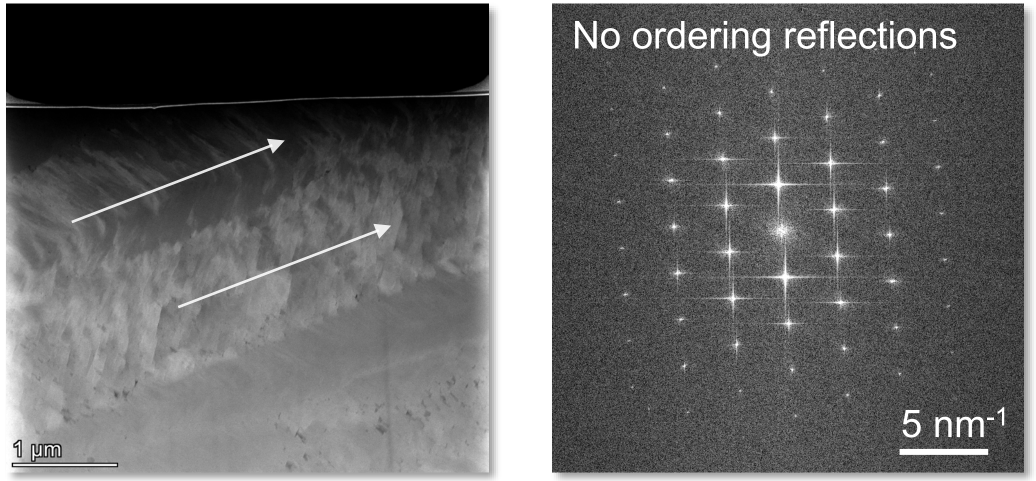
- Electron backscatter diffraction reveals a large uniform core and a granular rim
- Exotic Mg-deficient and ordered ankerite structure observed in the core region surrounded by spherulitic siderite
- Mg in all natural ankerite samples
- Ordered Mg-deficient ankerite not known synthetically or naturally.




**Ordered Ankerite Core Region**



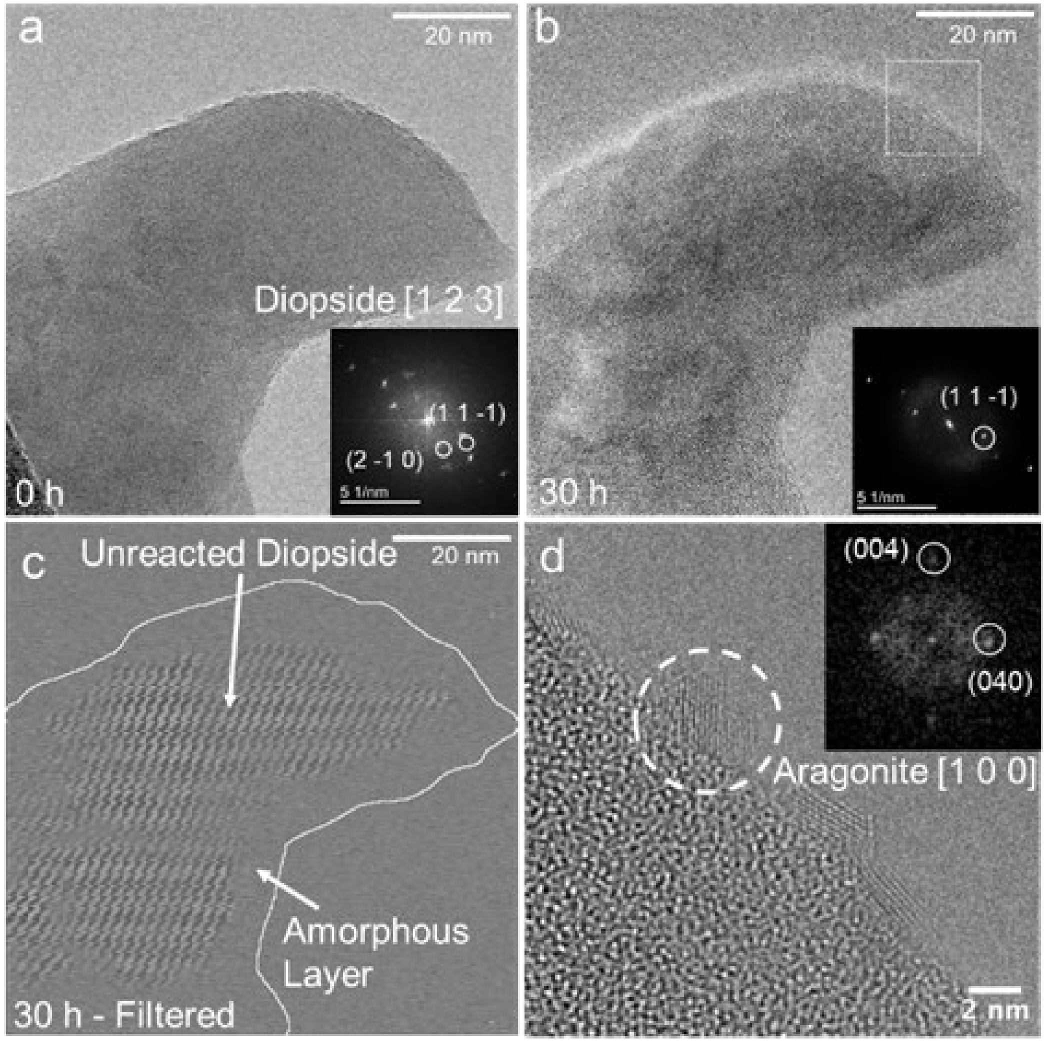

**Calcian Siderite Rim Region**




**Key Outcomes:**
Accurate identification of carbonate phases enables better predictive geochemical modeling and refinement of capacity estimates for future sequestration efforts in reactive reservoirs.

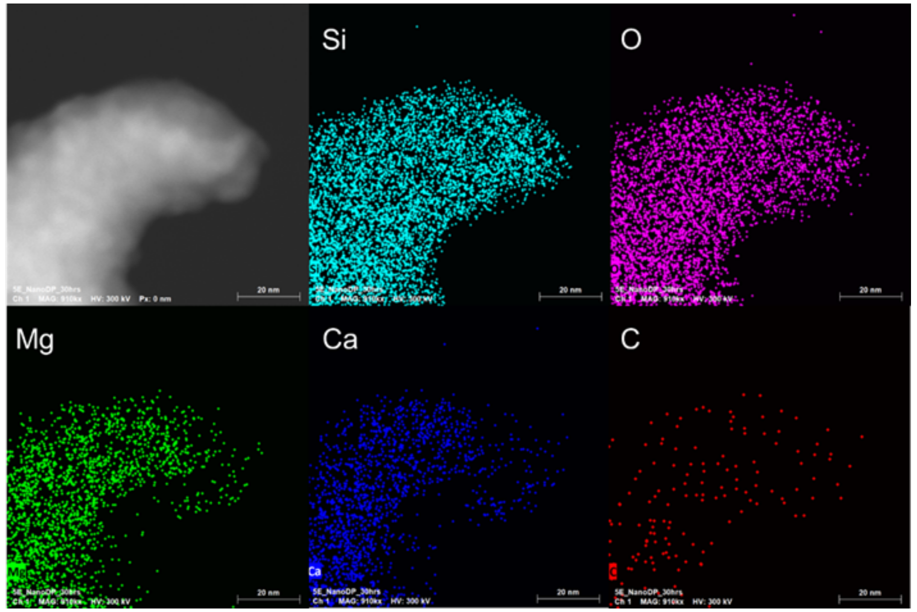


# Nanoscale Amorphous Phases Control Carbon Mineralization in Basalts




## Identical location TEM methodology reveals importance of amorphous precursors in carbon mineralization

- Diopside ($MgCaSi_2O_6$) [and Forsterite ($Mg_2SiO_4$)] show initial formation of amorphous material and volume expansions following reaction with $scCO_2$ (50 °C, 90 bar)
- Nanoscale aragonite ($CaCO_3$) then crystallizes on amorphous material, not directly from crystalline diopside.
- The amorphous layer is depleted in carbonate-forming cations compared to unreacted mineral.
- Mg is not incorporated into carbonate phases, consistent with previous lab- and field-scale data.



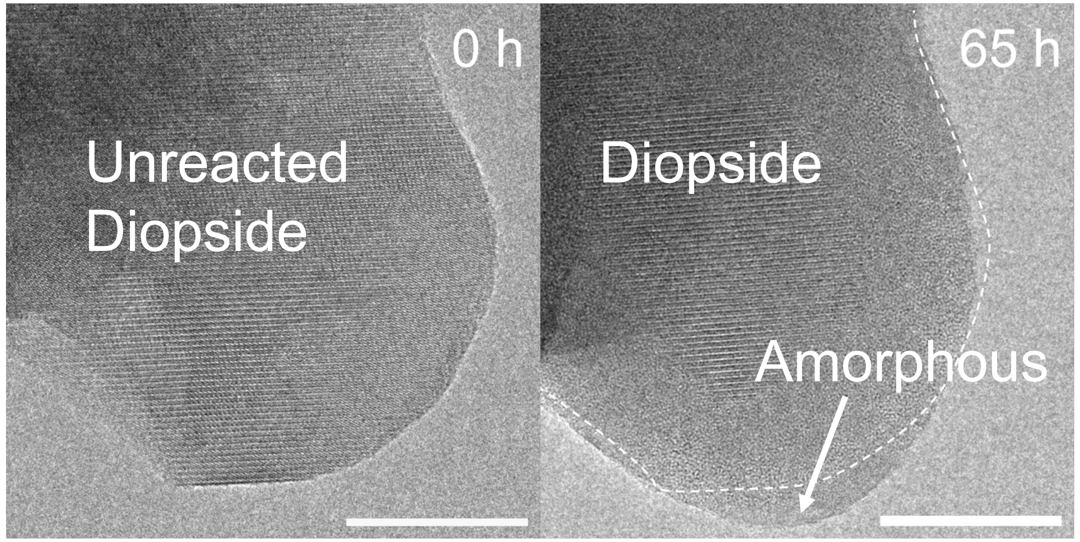

**Li et al., 2023, Identical location transmission electron microscopy reveals nanoscale intermediates during silicate carbonation in wet supercritical $CO_2$, *in preparation*.**

**Key Findings:**
- An amorphous phase depleted in cationic species is formed following reaction with wet supercritical $CO_2$.
- Nanoscale aragonite subsequently crystallizes on the reactive amorphous phase

# Influence of Biomineralization on Mineral Carbonation and Fate of Critical Materials

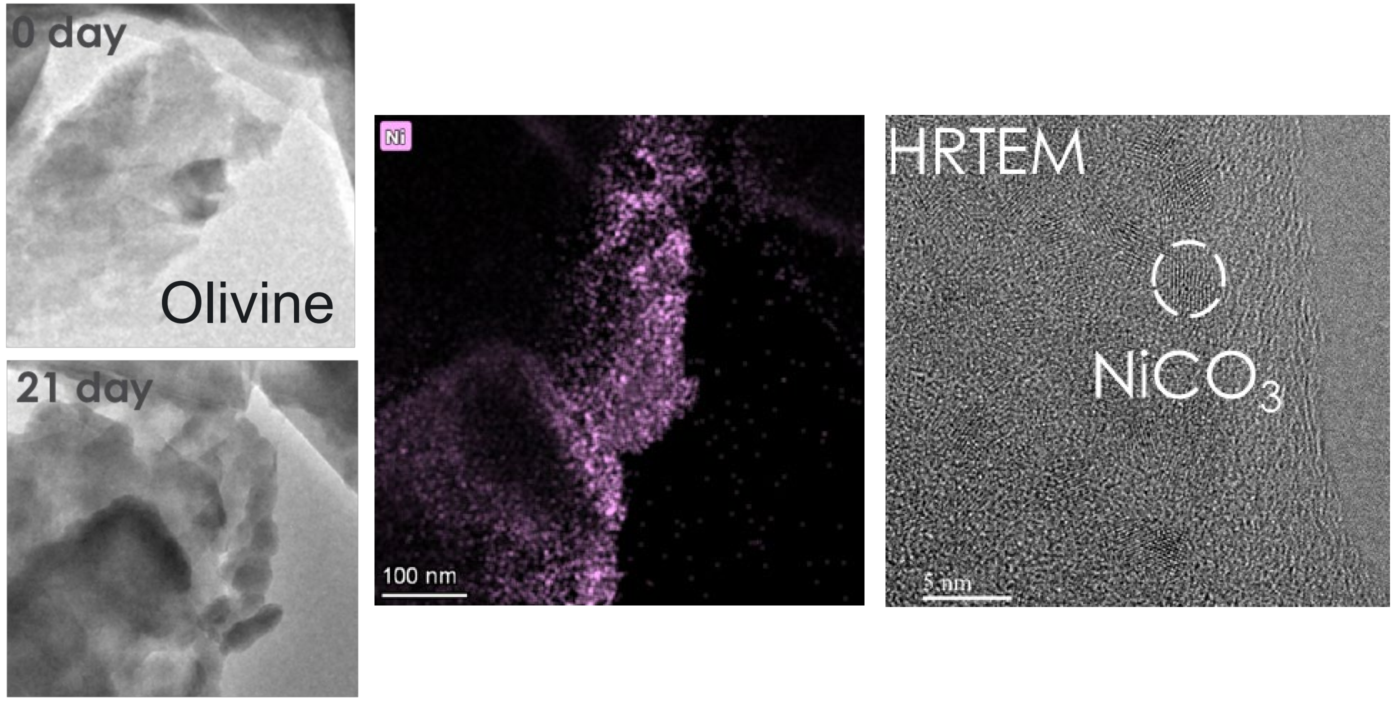
## The use of biomolecule proxies do not alter the short time scale and & molecular mechanisms behind carbon mineralization in silicate minerals

- Formation of amorphous layer on the surface of diopside is unchanged with the addition of citrate.
- Limited evidence of enhanced leaching of Mg and Ca from amorphous material.




## Identical location TEM reveals the fate of Ni in olivine following reaction with $scCO_2$

- Olivine forms a Ni-enriched amorphous layer upon reaction with $scCO_2$ (50°C, 90 bar).
- Ni is then incorporated into crystalline $NiCO_3$.




**Key Findings:**

- Primary formation of an amorphous material on mineral surface is common among all minerals tested, with secondary formation of crystalline carbonates, including those containing critical materials.
- Biomineralization does not appear to initially alter the mechanisms behind carbon mineralization.

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# Stakeholder and Community Outreach is Strategic for Clean Energy Project Acceptance and Developing STEM Pipeline

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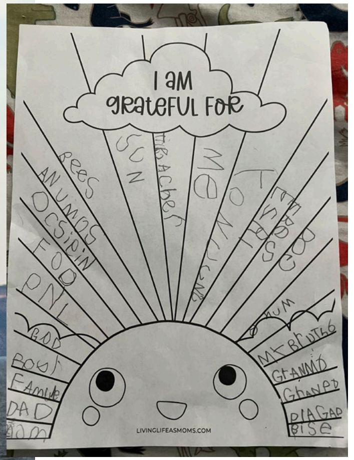
- Early inclusion of communities and stakeholders in clean energy projects is vital
- Early career researchers (e.g., interns, PDs, staff, visitors, etc.)
- DOE synergy: FECM (MLEF), SC (VFP, SULI, SCGSR), NNSA (MSIPP), CCI, GEM
- Nurturing sustainable STEM pipeline that fosters diversity and inclusivity




# Next Steps (FY24)

- Develop modeling tools that incorporate critical insights from field and laboratory studies
- Identify dominate fluid flow regimes to better minimize impacts to porosity and permeability
- Establish a baseline modeling approach, benchmarked by laboratory studies, to:
  - Simulate formation water recovery post $CO_2$ injection,
  - Support permitting efforts (e.g., class VI),
  - Develop engineered injection strategies (e.g., WAG, additives, critical mineral extraction, etc.) for restoring ground water chemistry to the natural state.
- Create and disseminate a reactive modeling tool that can simulate reactivity of water-bearing $scCO_2$ fluids in a reactive reservoir.

# Carbon Mineralization Research Portfolio at PNNL connects Fundamental Processes to Field Scale Deployment

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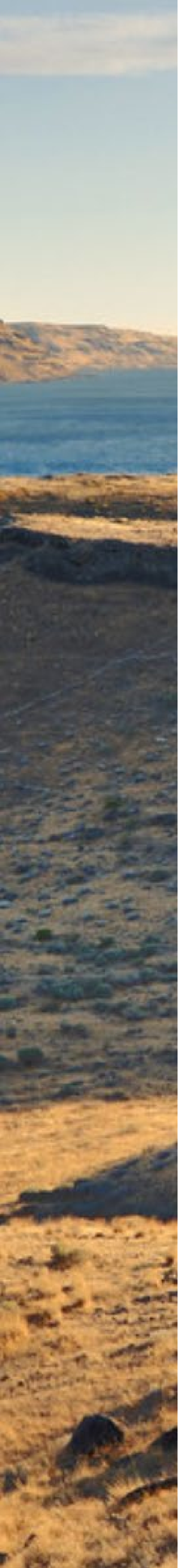
**Pore-scale to nanoscale studies** inform molecular mechanisms of carbonate nucleation and growth

**Reactive Transport Simulations** help derisk permitting and deployment of carbon storage at the field scale

Advanced **subsurface monitoring** and **deployment** technologies enable commercial-scale carbon sequestration in reactive reservoirs

**Tuesday (Aug 29) at 5:45pm at the Ballroom Foyer!**

# Appendix



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# Gantt Chart and Milestones for FY23

| Milestone | Description | QRT |
|---|---|---|
| **M1** | Downselect biomolecules to test in experiments based on the results of the critical literature review. | Q1 |
| **M2** | Initiate nano/micro-analysis of biogenic influences of Wallula carbonates | Q2 |
| **M3** | Compare experimental determinations of mineral carbonation kinetics with the compiled literature | Q3 |
| **M4** | Submit journal article detailing critical mineral behavior and reaction rates for carbon biomineralization at subsurface conditions in the context of the broader critical literature review and Wallula SWC insights. This milestone will be produced using information from all four tasks. | Q4 |

| | | | | | | FY23 | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Task** | **Milestone** | **Title** | **G/N** | **Begin** | **End** | **Q1 1** | **Q2 2** | **Q3 3** | **Q4 4** |
| | | **Sequestration in Basalt Formations FWP 73235** | | 0 | 4 | ■ | ■ | ■ | ■ |
| Task 1 | | *Biomineralization Literature Review* | | | | | | | |
| | M1 | Downselect biomolecules to test in experiments based on the results of the critical literature review. | | 1 | 1 | ▲ | | | |
| Task 2 | | *Biosignatures of Natural and Anthropogenic Wallula Carbonates* | | | | | | | |
| | M2 | Initiate nano/micro-analysis of biogenic influences of Wallula carbonates | | 2 | 3 | | ▲ | | |
| Task 3 | | *Biomolecule Enhancement of Carbonation* | | | | | | | |
| | M3 | Compare experimental determinations of mineral carbonation kinetics with the compiled literature | | 3 | 3 | | | ▲ | |
| Task 4 | | *Critical Mineral Outcomes During Carbonation* | | | | | | | |
| | M4 | Submit journal article detailing critical mineral behavior and reaction rates for carbon biomineralization at subsurface conditions in the context of the broader critical literature review and Wallula SWC insights. | | 4 | 4 | | | | ▲ |

# Summary of Lessons Learned

| Lesson Learned | Supporting Information |
|---|---|
| Injected supercritical $CO_2$ (dry) in contact with water is reactive. | Findings from WBPP reveal carbonation occurred during the 24-month period that was directly linked to the injected $CO_2$. Minerals identified in the sidewall cores include ankerite, siderite, aragonite, and zeolite. |
| Pre and post comprehensive hydrogeological characterization conducted on the target injection zones is critical. | Detailed analysis of pre- and post-injection hydrologic tests that capitalizes on the difference in fluid properties between $scCO_2$ and water can be used to assess changes in near-field, wellbore, and reservoir conditions. |
| Reactive reservoir simulations of $CO_2$-water-basalt interactions at WBPP are complex and rely on post carbonate characterization. | Paragenetic insights for the timing of aragonite, silica, and fibrous zeolites are captured in sidewall cores retrieved post $CO_2$ injection. These samples provided clarification, based on mineral texture and spatial relationships, along with time-resolved downhole fluid sampling, on the mineralogy, chemistry, and paragenesis of carbon mineralization. |