CO_2 Mineralization Storage in Basalt Reservoirs

Presented By

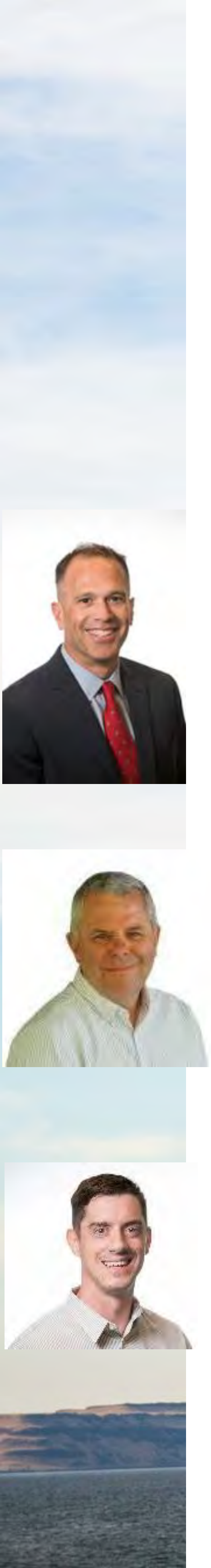
H. Todd Schaef

Senior Research Scientist

2022 CUSP Annual Meeting

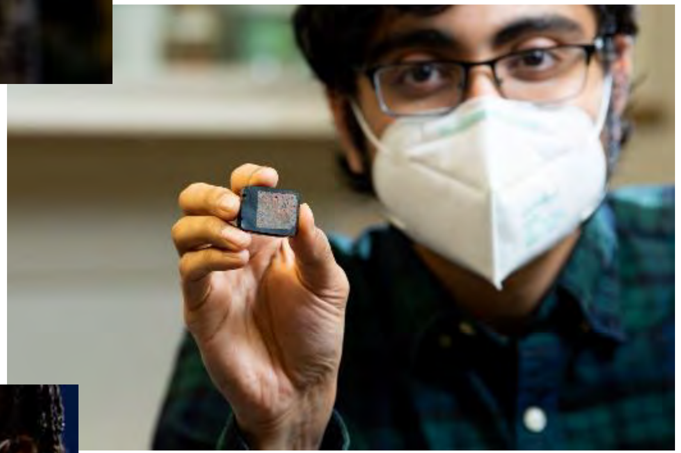
PNNL is operated by Battelle for the U.S. Department of Energy

Photo: Andrea Starr (PNNL



Presentation Outline

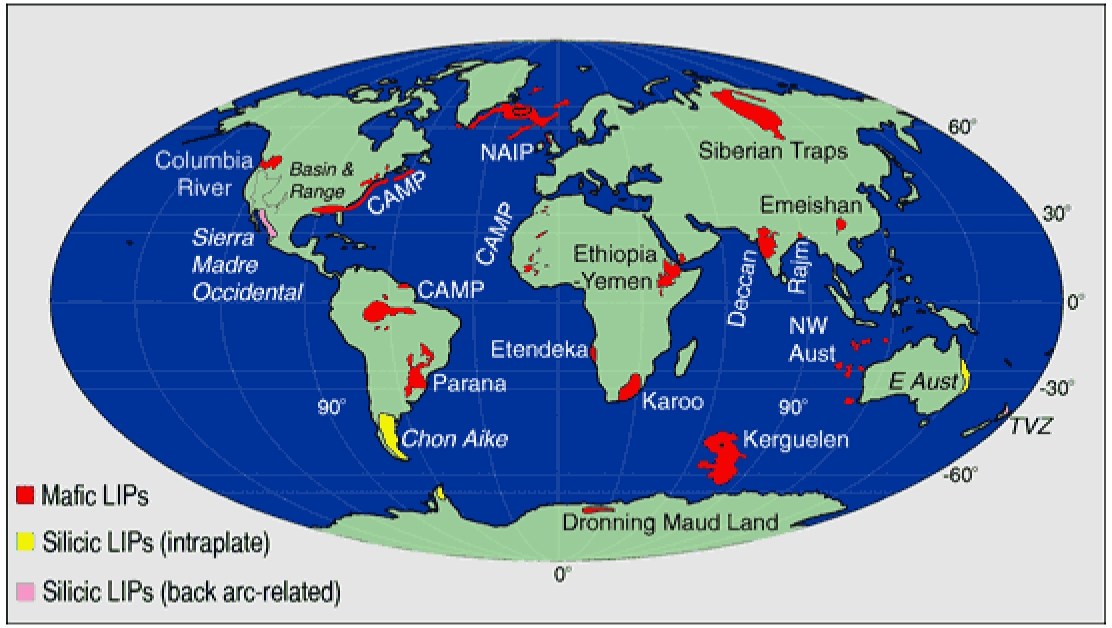
- Storing CO_2 in Basalt Formations
  - Reasons for sequestering carbon in basalts
  - Unique basalt characteristics
- Laboratory Based Studies
  - Basalt carbonation
- Field Study Demonstration in Wallula, WA
  - Project background
  - Side wall core analysis
- Summary and Perspective
  - What we know from laboratory and field studies
  - Barriers and gaps needing addressed
- Part II: Multiphase Reservoir Simulations (Mark White)
- Part III: Early Career Contributions and Research Frontiers (Quin Miller)



Why Sequester Carbon in Basalts?

Favorable Attributes of Basalt

- Highly reactive with supercritical CO_2
- Self-sealing for leakage scenarios
- Common rock type with worldwide distribution
- Flood Basalt = large volumetric thickness



Major basalt formations can be found on every continent, offshore, and in the deep sea.

McGrail, Schaef et al 2006, “Potential for CO_2 Sequestration in Flood Basalts”, Journal of Geophysical Research, Vol 111, B12201.

Continental flood basalts are layered structures that serve as regional aquifers in parts of the world.

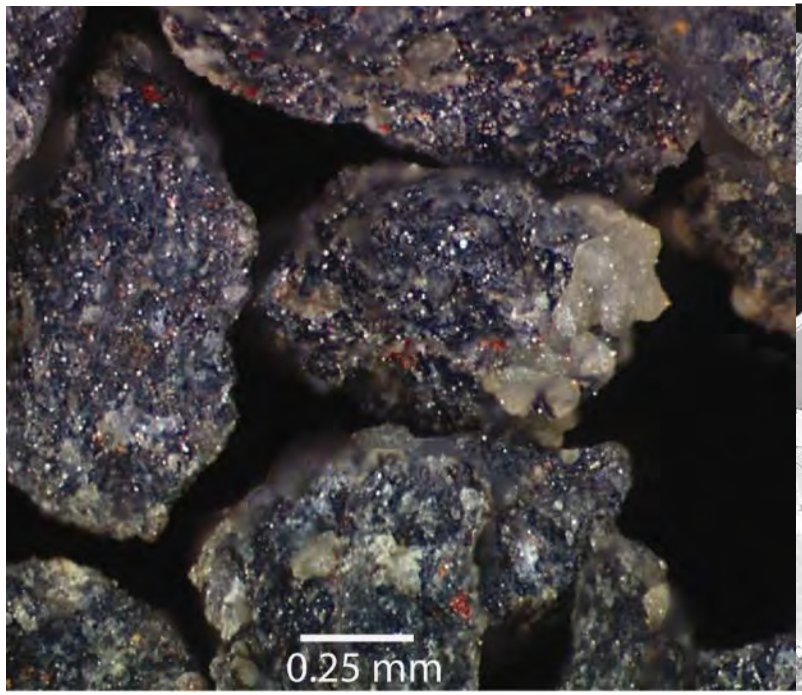
Discrete Carbonation Products Form Through Exposing Basalt Chips with CO_2-Water

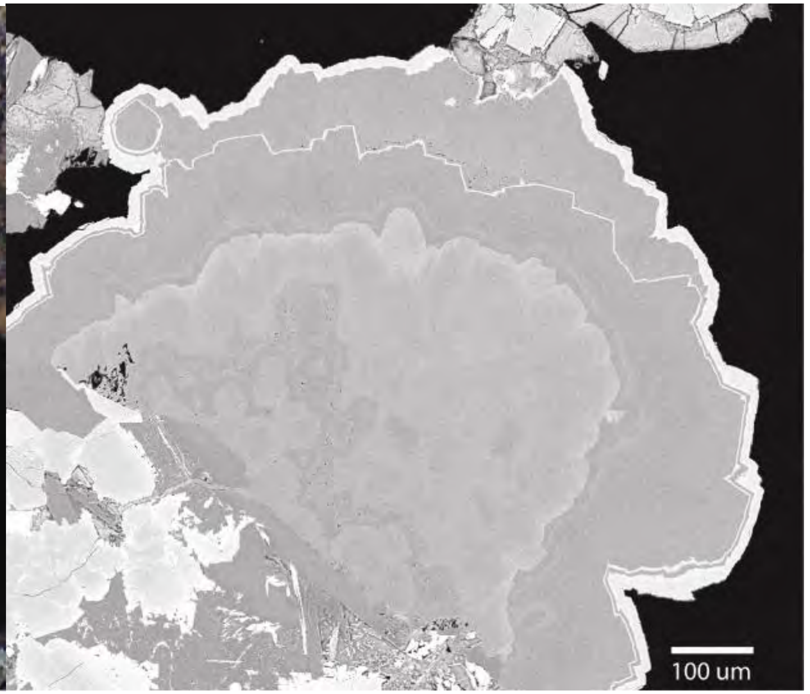
Experimental Derived Data

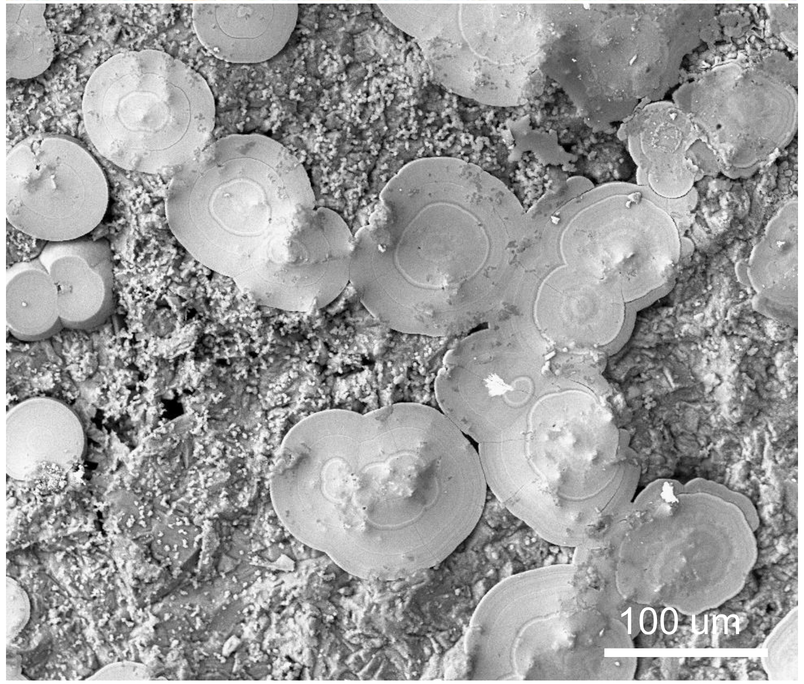
- reaction products
  - Calcite
  - Aragonite
  - Rhodochrosite
  - Ankerite
- variable chemistry
  - Heavily substituted with Fe^{2+}, Mn^{2+}, and Mg^{2+}
- carbonate structure transitions with depth
- estimated carbonate rate
  - ~0.19 kg m^{-3} yr^{-1}

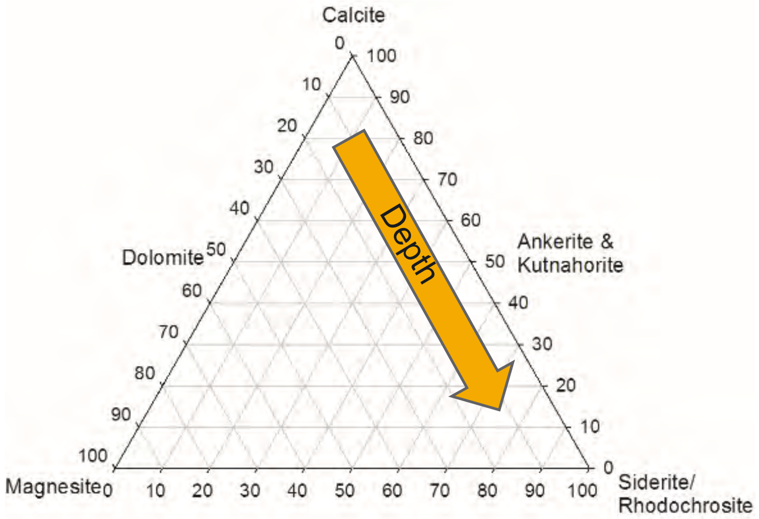
Schaef, McGrail, et al 2010, “Carbonate mineralization of volcanic province basalts”, IJGGC, 1 249-261.

Xiong, Wells, Horner, Schaef, et. al., 2019. “Potential for CO_2 Sequestration in Flood Basalts”, Journal of Geophysical Research, Vol 111, B12201.

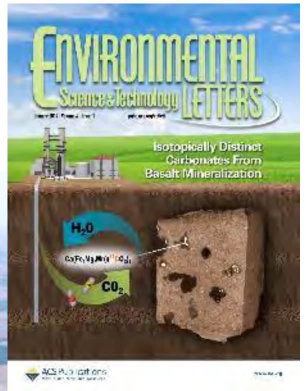








Wallula Basalt Carbon Sequestration Pilot Project Injected 977 MT of CO_2 829 m Below Surface



Project Background:

- Drilling initial test characterization and well completion: Jan. – May 2009
- Injection permit issued: March 2011
- Extended hydraulic test characterization: Sept. – Nov. 2012
- ~1,000 MT CO_2 injection: July 17^{th} – August 11^{th}, 2013
- Post-injection air/soil monitoring and downhole fluid sampling performed for ~2 years following injection
- Final well characterization activities: June – July 2015
- Detailed wireline survey/Extended hydrologic tests/Sidewall Core
- Final well decommissioning/site demobilization: August 2015
- Reservoir Simulations (2020)
- **Current Status:**
- Sidewall core characterization (2017-present)

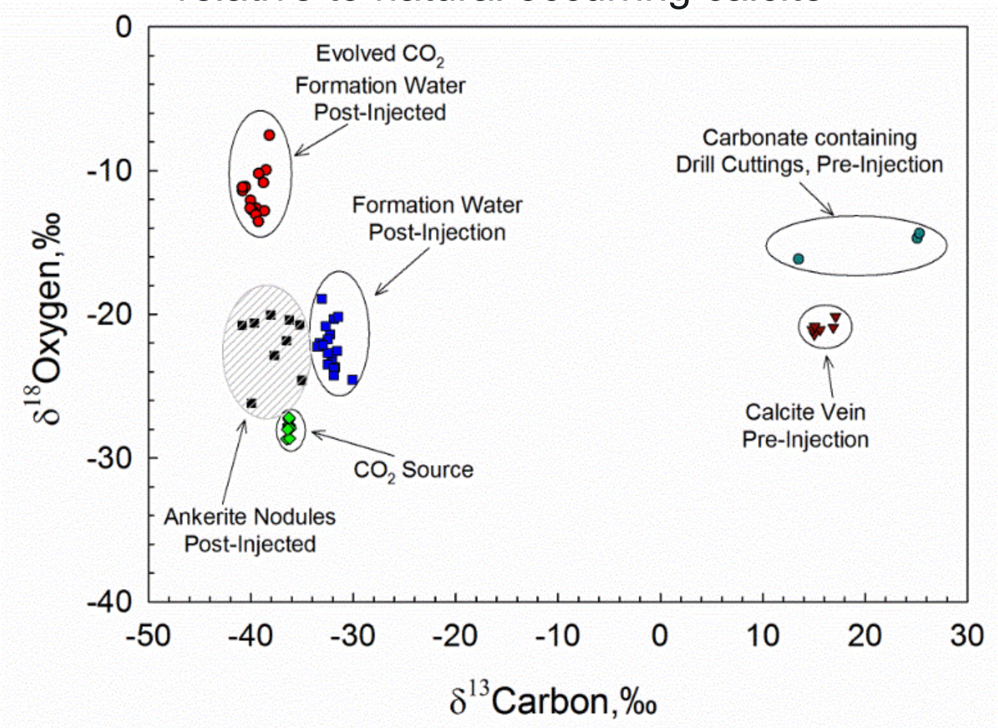
McGrail, Schaef et al 2017, "Wallula Basalt Pilot Demonstration Project: Post-Injection Results and Conclusions", Energy Procedia, 114, 5783-5790.

Sidewall Core Characterization Revealed Ankerite as forming CO_2 post injection

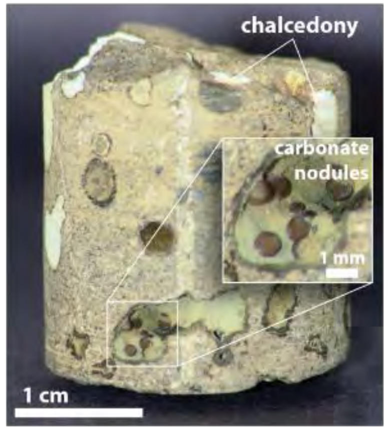
Pacific Northwest NATIONAL LABORATORY

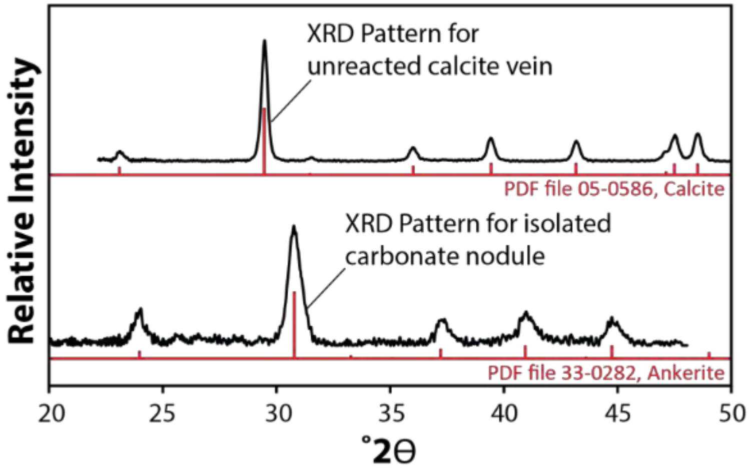
- 50 sidewall cores (SWC) were collected across the open borehole section between 827.8 to 883.9 m (2,716 – 2,900 ft bgs)
- Carbonate nodules observed on SWCs occurred both as large (up to ~1mm) nodules as a coating (cements)
- XRD of nodule material identified ankerite
- Isotopic signature confirmed the injected CO_2 was mineralized

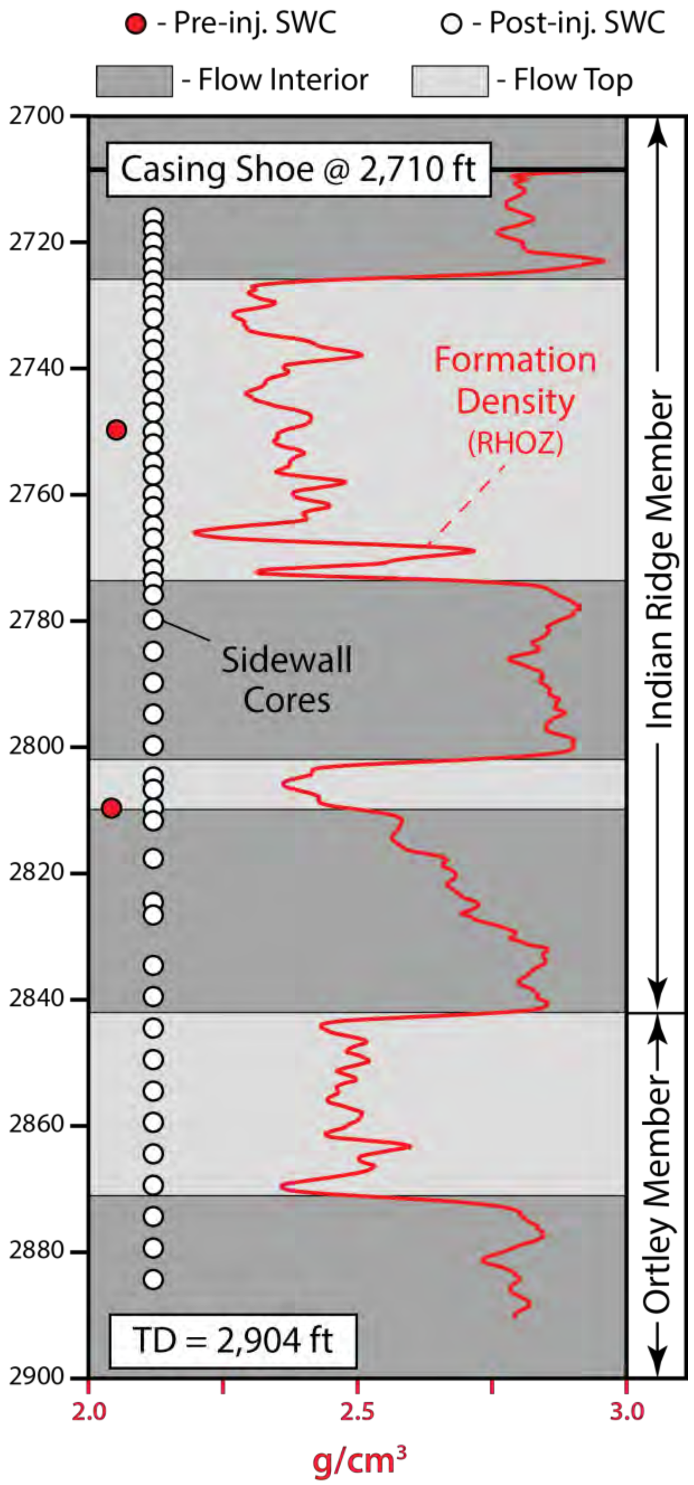
Ankerite nodules were depleted in $\delta^{13}C$ relative to natural occurring calcite



SWC Sample



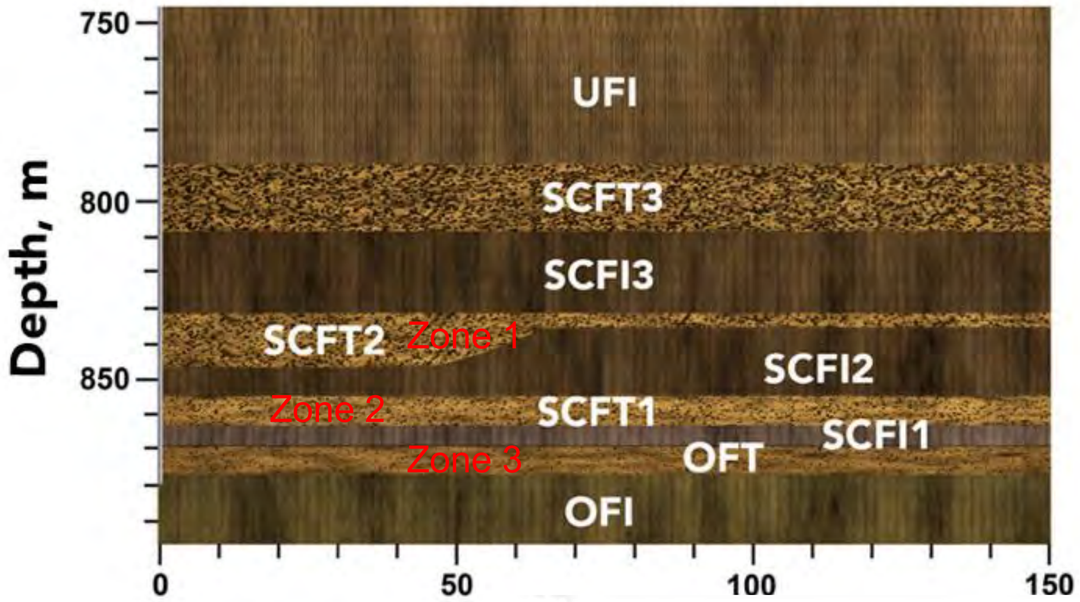




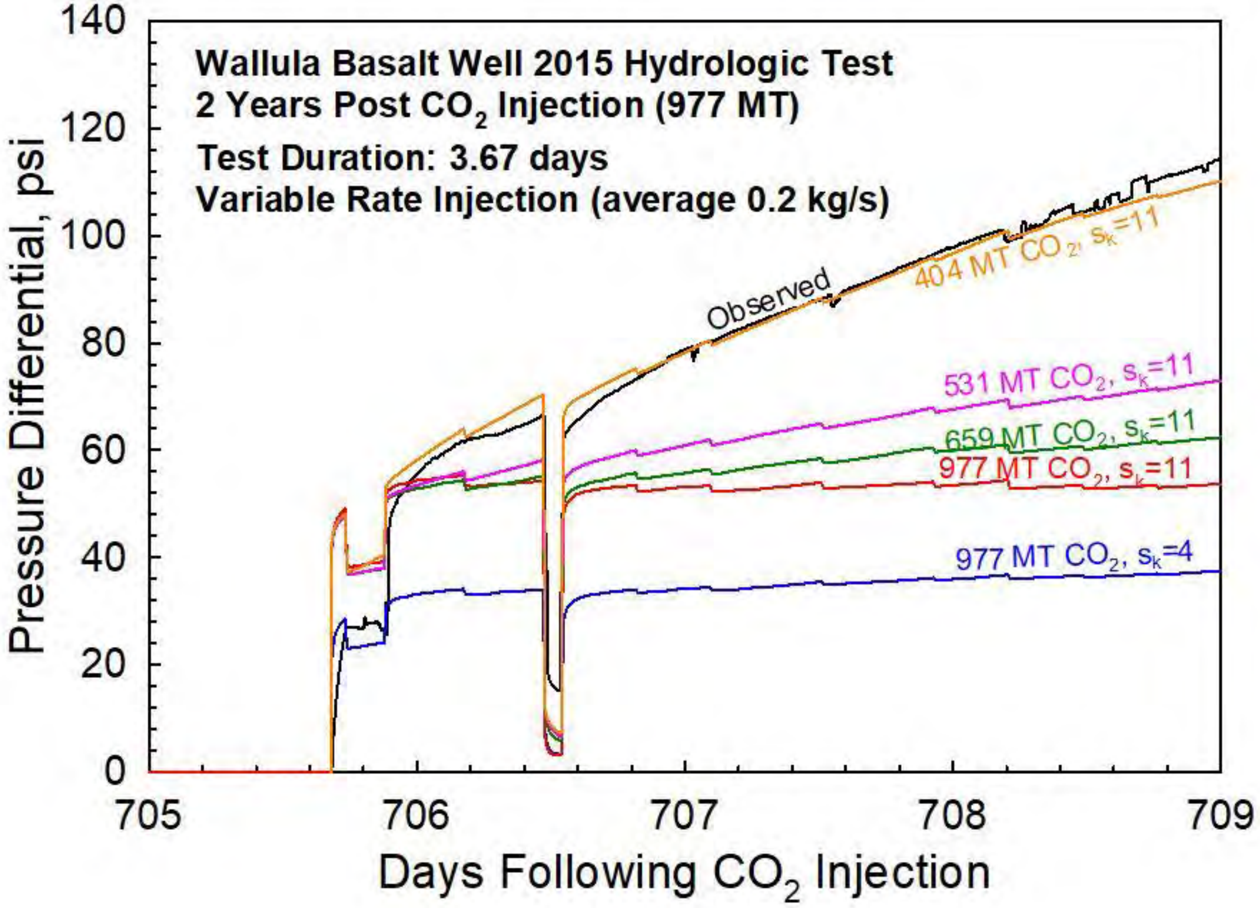
McGrail, Schaef, et al. 2017. "Field Validation of Supercritical CO_2 Reactivity with Basalts." *ES&T, Letters, 4, 6-10.*

Field-Scale Reservoir Simulations Indicate ~60% (~600 tones) of CO_2 is Converted in 24 Months

Layered basalt model properties identified from the 2012 pre-injection hydrologic test

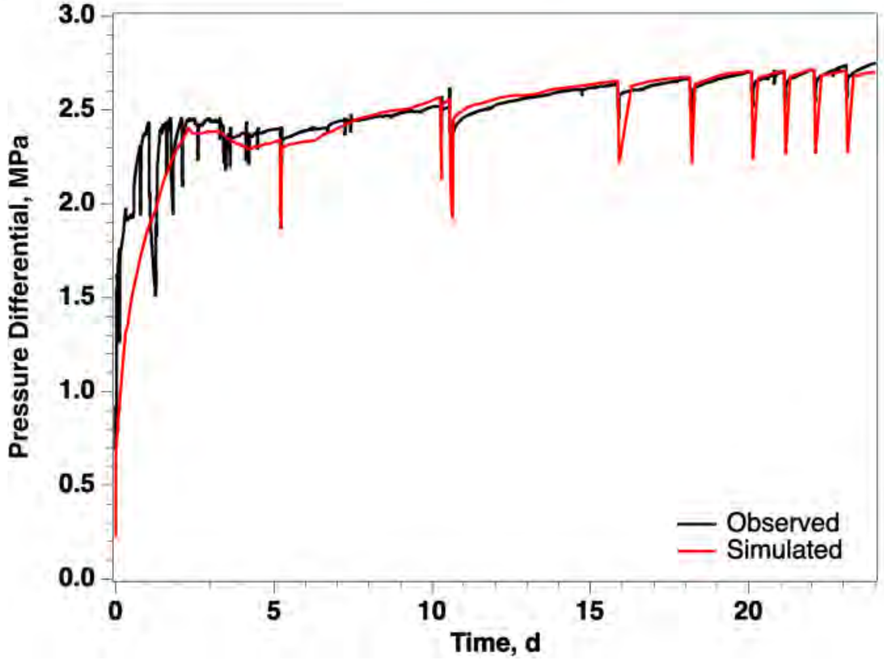


Post-injection pressure testing: STOMP-CO2 reservoir simulation of post-injection pressure response with ~40% of residual CO_2 mass in the reservoir together with an increase in well skin (S_K) provided a near perfect match to observed reservoir response



Pressure injection response

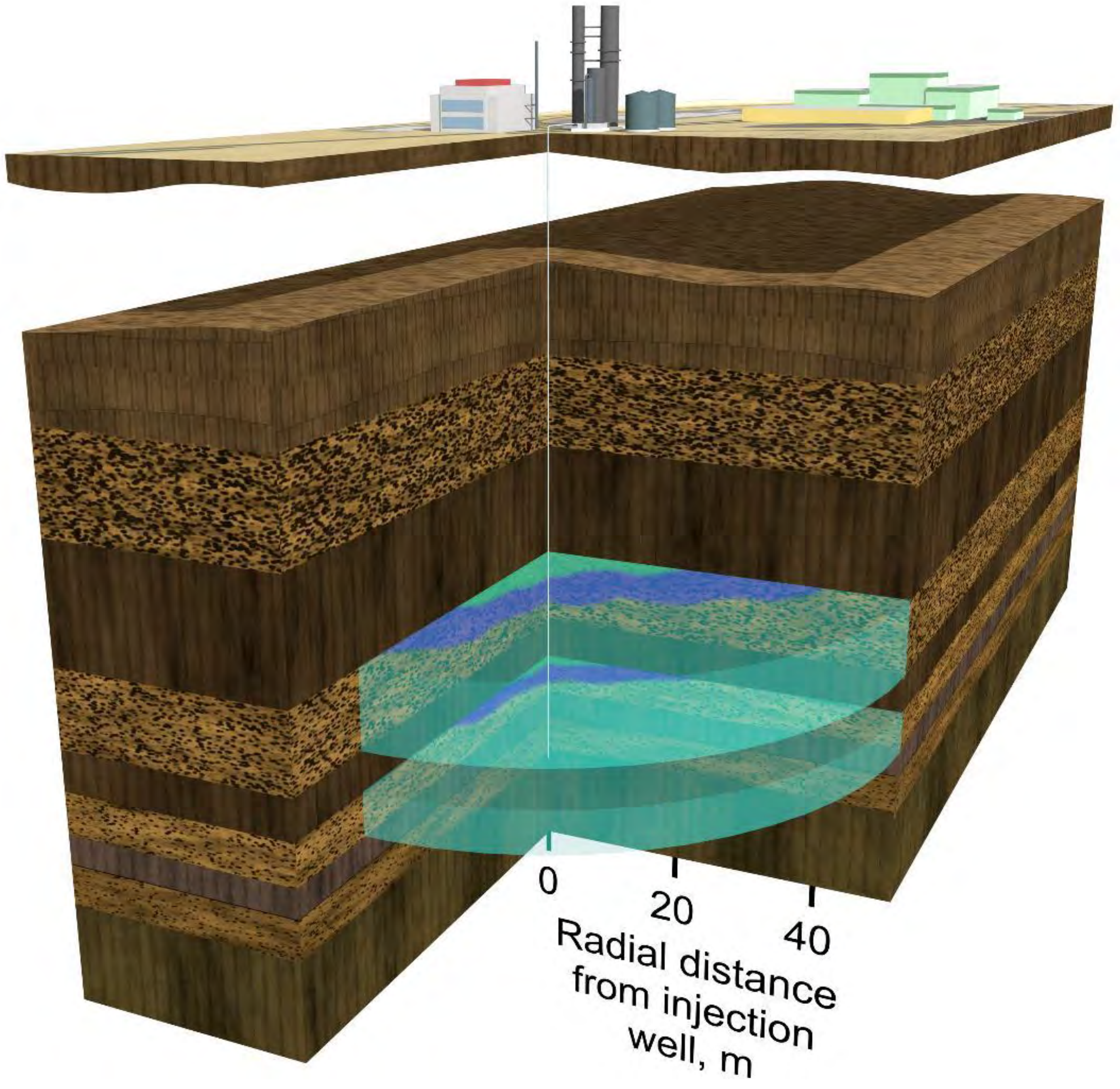
Simulated and observed pressure buildup responses (2013 CO_2 injection) matched



SK White, FA Spane, HT Schaef, et al., 2020. "Quantification of CO_2 Mineralization at the Wallula Basalt Pilot Project." *ES&T, 54, 14609-14616.*

Perspective on CO_2 Sequestration in Basalts

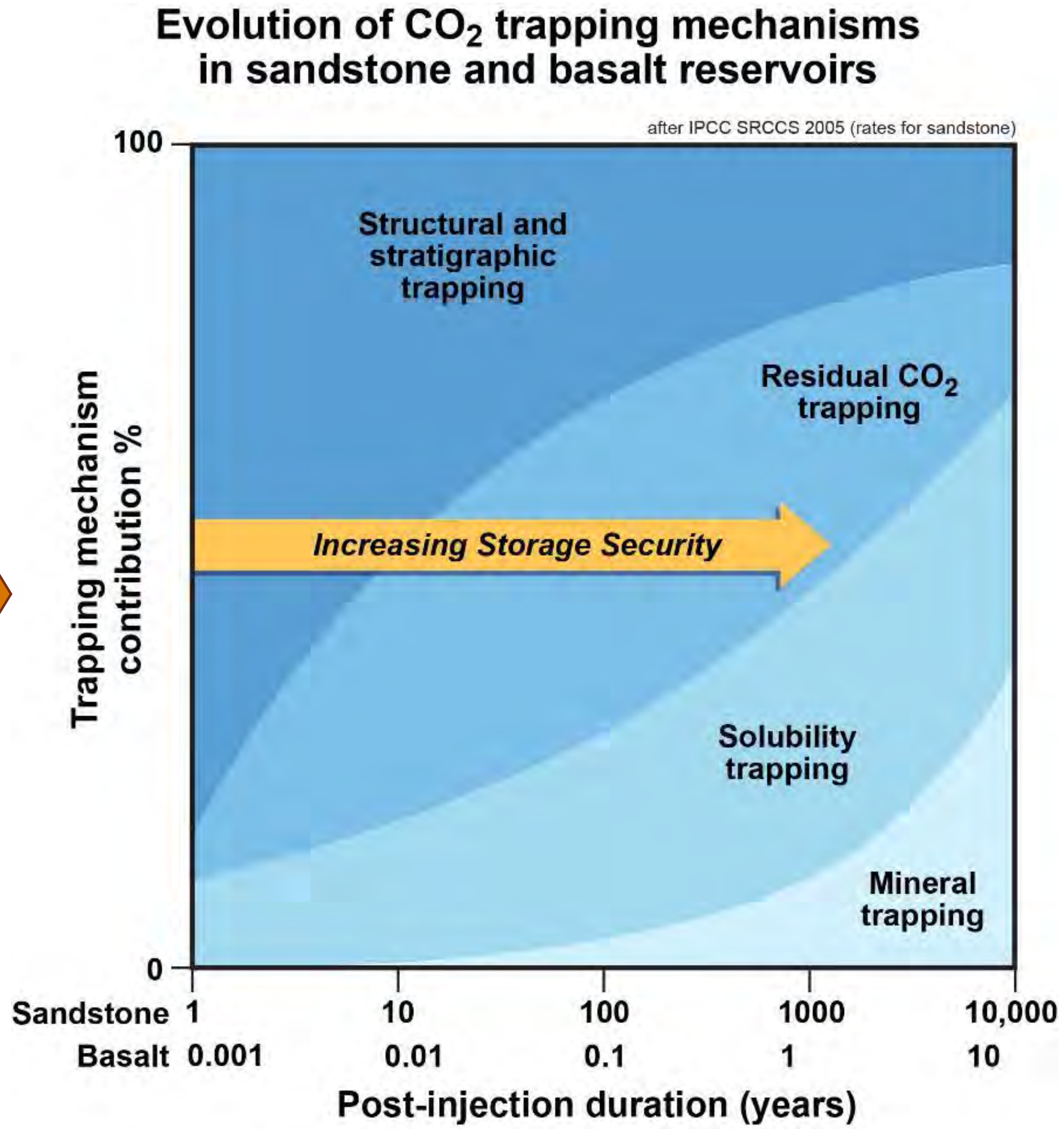
- Laboratory studies confirmed rapid carbonation
- First field evidence of *in situ* carbonation occurring from a free phase supercritical CO_2 injection into a flood basalt reservoir
- Hydrologic modeling approach for tracing extent of mineralization
- Basalt systems offer the most realistic chance of a paradigm shift in the conventional view of risk profile of CCS



Derisking Carbon Storage with Basalts

Address Gaps/Barriers to Commercialization

- Field derived mineralization rates are faster than laboratory values
- Impacts on porosity and permeability around a well and at the formation scale are unknown
- Estimating storage capacity, injection rates, and fluid migration at scale is difficult
- Detecting, and surveying injected fluids at reservoir scale is challenging in layered basalts.

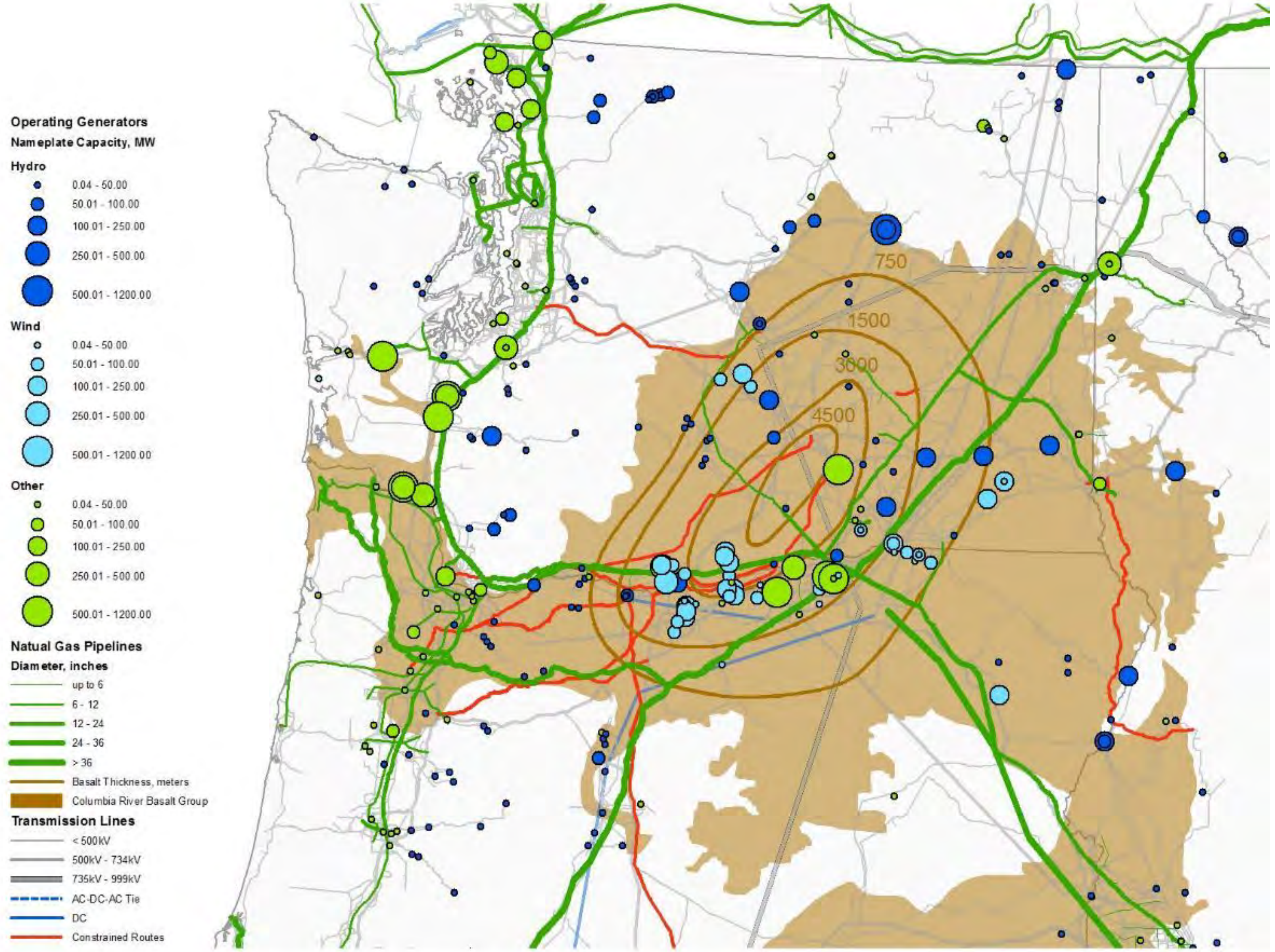


Basalts **convert CO_2 to solid minerals** much more rapidly than other rock types. Mineralized CO_2 is immobile and poses **no risk of leakage.**

Carbon Storage Opportunities in PNW: How do we build a business case?

Identify and evaluate carbon loop market actors

- Industrial CO_2 sources (e.g., stream purity, rate, fuel/feedstock source)
- Existing demand for CO_2 (e.g., requisite purity, rate, current market price for CO_2)
- Potential CO_2 utilization opportunities (e.g., requisite CO_2 purity, rate, finished commodity pricing)
- Geologic CO_2 storage resources (e.g., total storage potential, per-ton levelized storage cost)
- CO_2 utilization and storage incentives (e.g., 45Q tax credits, tradeable offset credits, RECs)



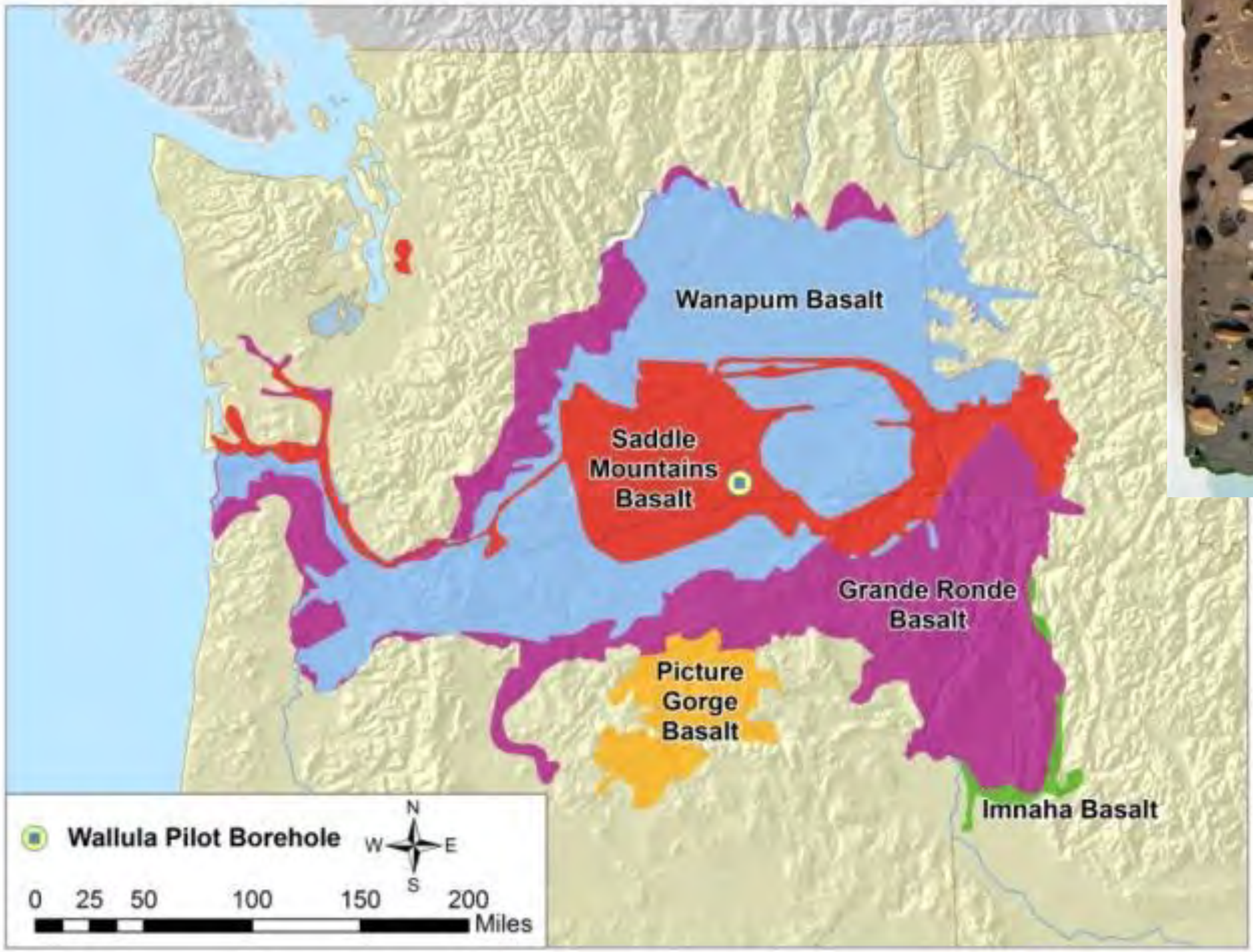
Key infrastructure, existing generation, and extent of the CRBG in the PNW. Contours are depths of basalt in meters.

Part 1 Summary

- **Climate change is a long-term strategic problem with implications for today**
- **CSS *may* have an important role in overall climate change policy**
- **Laboratory Studies Confirmed Rapid Carbonation when basalts from around the world exposed to scCO_2**
- **First field evidence of *in situ* carbonation occurring from a free phase supercritical CO_2 injection into a flood basalt reservoir**
  - Injection of 977 metric tons occurred August 2013
  - Final characterization campaign prior to decommissioning in July 2015
  - Detailed wireline survey characterization and groundwater samples for detecting the presence/migration of CO_2
  - Carbonates recovered post CO_2 injection
  - Reservoir simulations indicate ~60% CO_2 consumed through mineral carbonation
- **Validation of rapid carbonation rates that were first envisioned >15 years ago**

Preliminary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- Well depth of 4110 ft (1253 m)
- Slack Canyon #2 flow top
  - top 2720.5 ft (829 m)
  - bottom 2768.5 ft (844 m)
  - thickness 48.0 ft (14.6 m)
  - 70 mD permeability
  - 0.1 porosity
- Basalt Minerals
  - Plagioclase 37.4% (vol.)
  - Clinopyroxene 19.1% (vol.)
  - Glass 42.5% (vol)
  - Magnetite 1.1% (vol)
- Secondary Carbonates
  - Anatase
  - Beidellite-Ca, -K, -Mg
  - Calcite
  - Chalcedony
  - Dawsonite
  - Magnesite
  - Rhodochrosite
  - Siderite



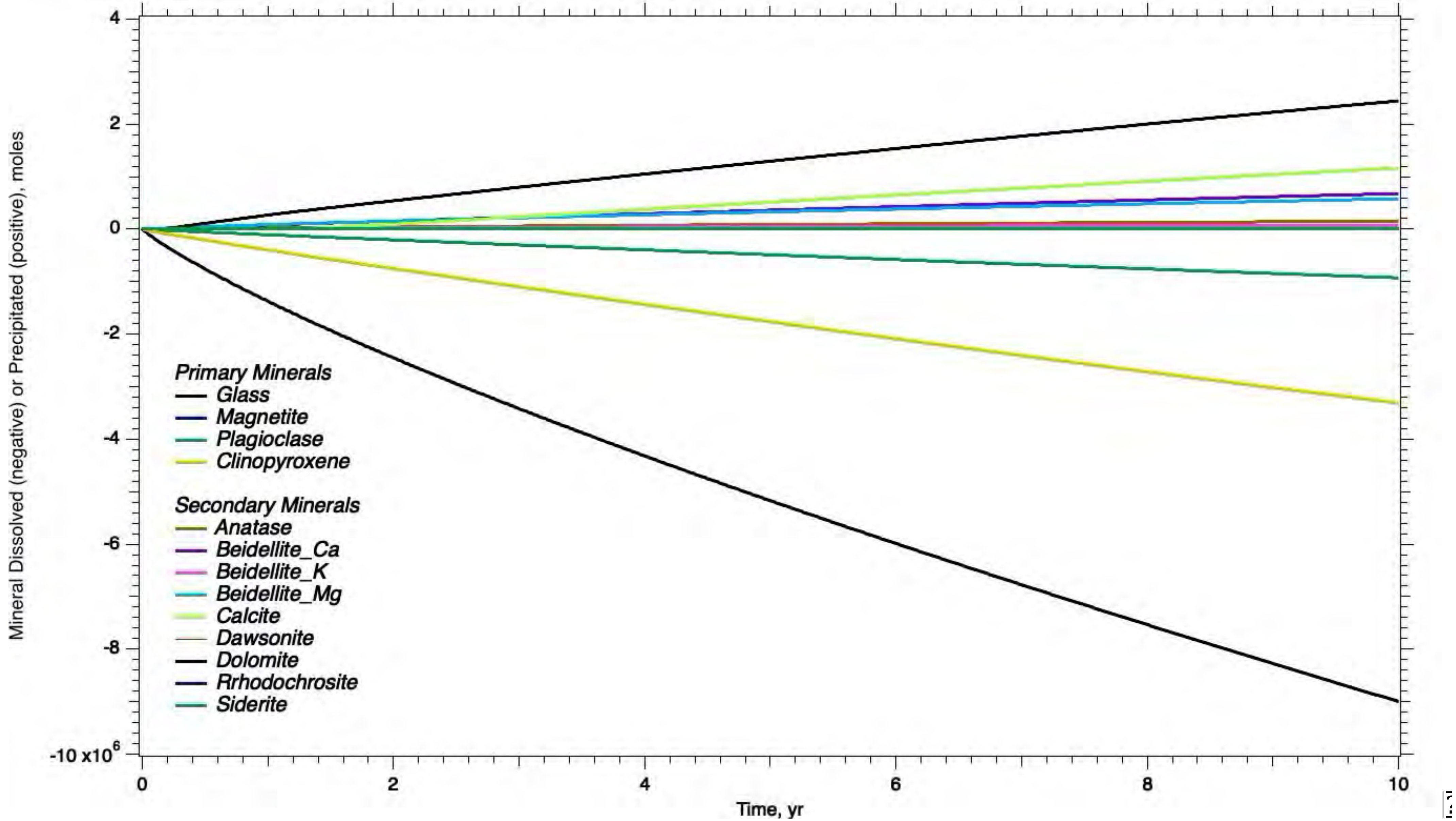
Preliminary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

Reaction	log K_{eq}	k_{ref} at T_{ref}, mol m^{-2} s^{-1}	T_{ref}, °C	E_a, kJ mol^{-1}	h
Plagioclase + 6.186H^+ = 1.5465Al^{3+} + 0.4535Na^+ + 3.093H_2O + 2.4535SiO_2 + 0.5465Ca^{++}	15.29	8.03×10^{-08}	60	42.1	0.626
Clinopyroxene + 4H^+ = Ca^{2+} + 0.25Fe^{2+} + 0.75Mg^{2+} + 2H_2O + 2SiO_2(aq)	19.89	4.13×10^{-06}	60	78.0	0.700
Glass + 0.8869H^+ = 0.429H_2O + 0.2051Al^{3+} + 0.0378Ca^{2+} + 0.0364Fe^{2+} + 0.0329K^+ + 0.0049Mg^{2+} + 0.0056Mn^{2+} + 0.0693Na^+ + SiO_2(aq) + 0.007Ti(OH)4(aq)	-2.60	3.93×10^{-08}	100	30.3	0.318
Magnetite + 6H^+ = 3Fe^{2+} + 0.5O_2(g) + 3H_2O	-5.15	8.34×10^{-11}	60	18.6	0.279

Reaction	log K_{eq}	k_{ref} at T_{ref}, mol m^{-2} s^{-1}	T_{ref}, °C	E_a, kJ mol^{-1}	h
Anatase + 2H_2O = $Ti(OH)_4$(aq)	9.65	4.47×10^{-09}	25	37.9	0.421
Beidellite-Ca + 7.32H^+ + = 0.165Ca^{2+} + 2.33Al^{3+} + 3.67SiO_2(aq)	4.65	1.05×10^{-11}	25	23.6	0.340
Beidellite-K + 7.32H^+ = 0.33K^+ + 2.33Al^{3+} + 3.67SiO_2(aq)	4.43	1.05×10^{-11}	25	23.6	0.340
Beidellite-Mg + 7.32H^+ + = 0.165Mg^{2+} + 2.33Al^{3+} + 3.67SiO_2(aq)	4.60	1.05×10^{-11}	25	23.6	0.340
Calcite + H^+ = Ca^{2+} + HCO_3^-	1.70	5.01×10^{-01}	25	14.4	1.000
Chalcedony = SiO_2(aq)	-3.56	5.89×10^{-13}	25	74.5	0.000
Dawsonite + 3H^+ = Al^{3+} + Na^+ + HCO_3^-	3.91	1.00×10^{-07}	25	62.8	0.000
Magnesite + H^+ = Mg^{++} + HCO_3^-	2.04	4.17×10^{-07}	25	14.4	1.000
Rhodochrosite + H^+ = HCO_3^- + Mn^{2+}	-0.32	1.02×10^{-03}	25	21.0	0.900
Siderite + H^+ = Fe^{2+} + HCO_3^-	-0.38	1.02×10^{-03}	25	21.0	0.900

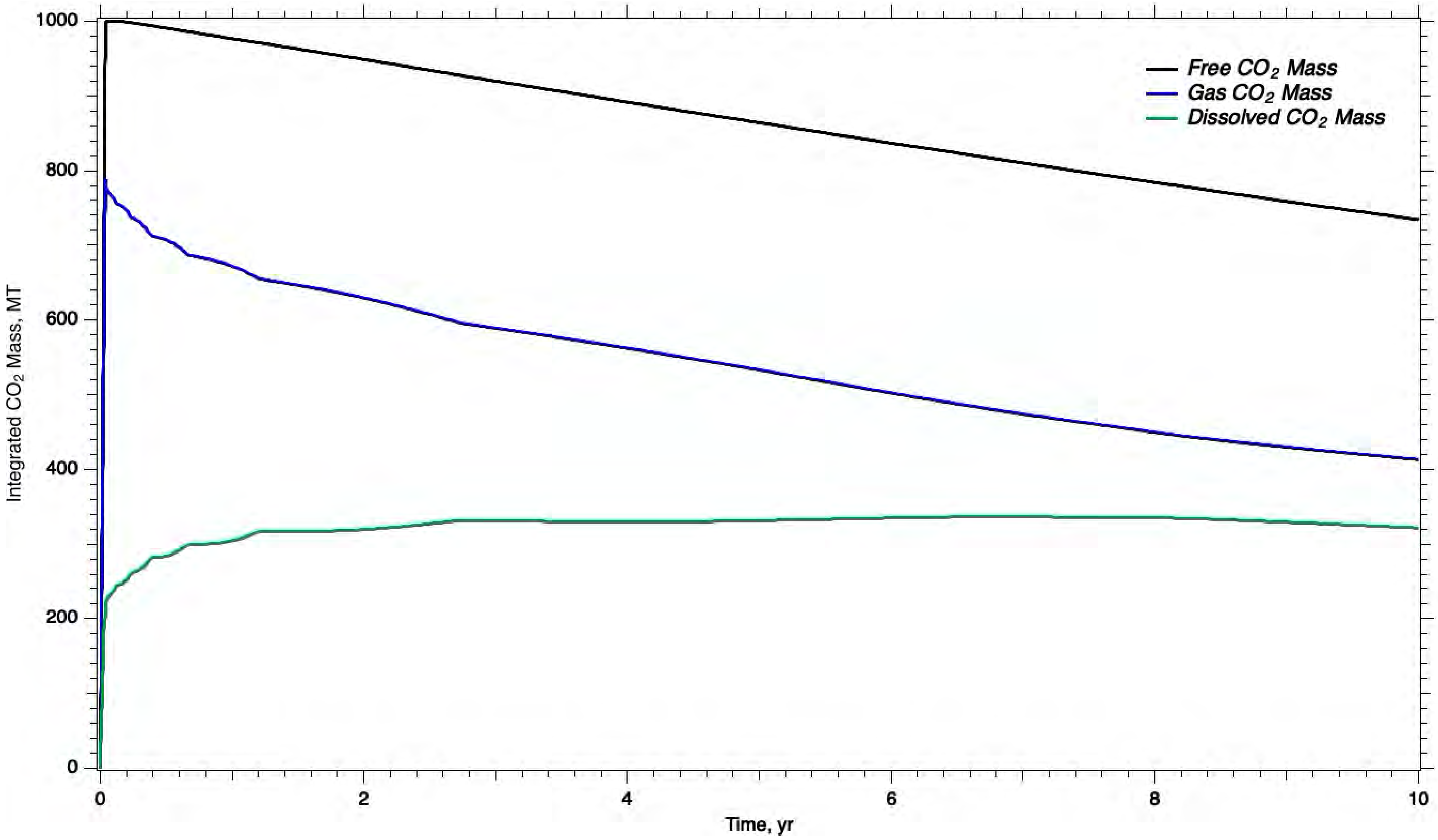
$$r = k_{ref} A \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]\left(1 - \frac{Q}{K_{eq}}\right)10^{(-h\ pH)}$$

Preliminary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)



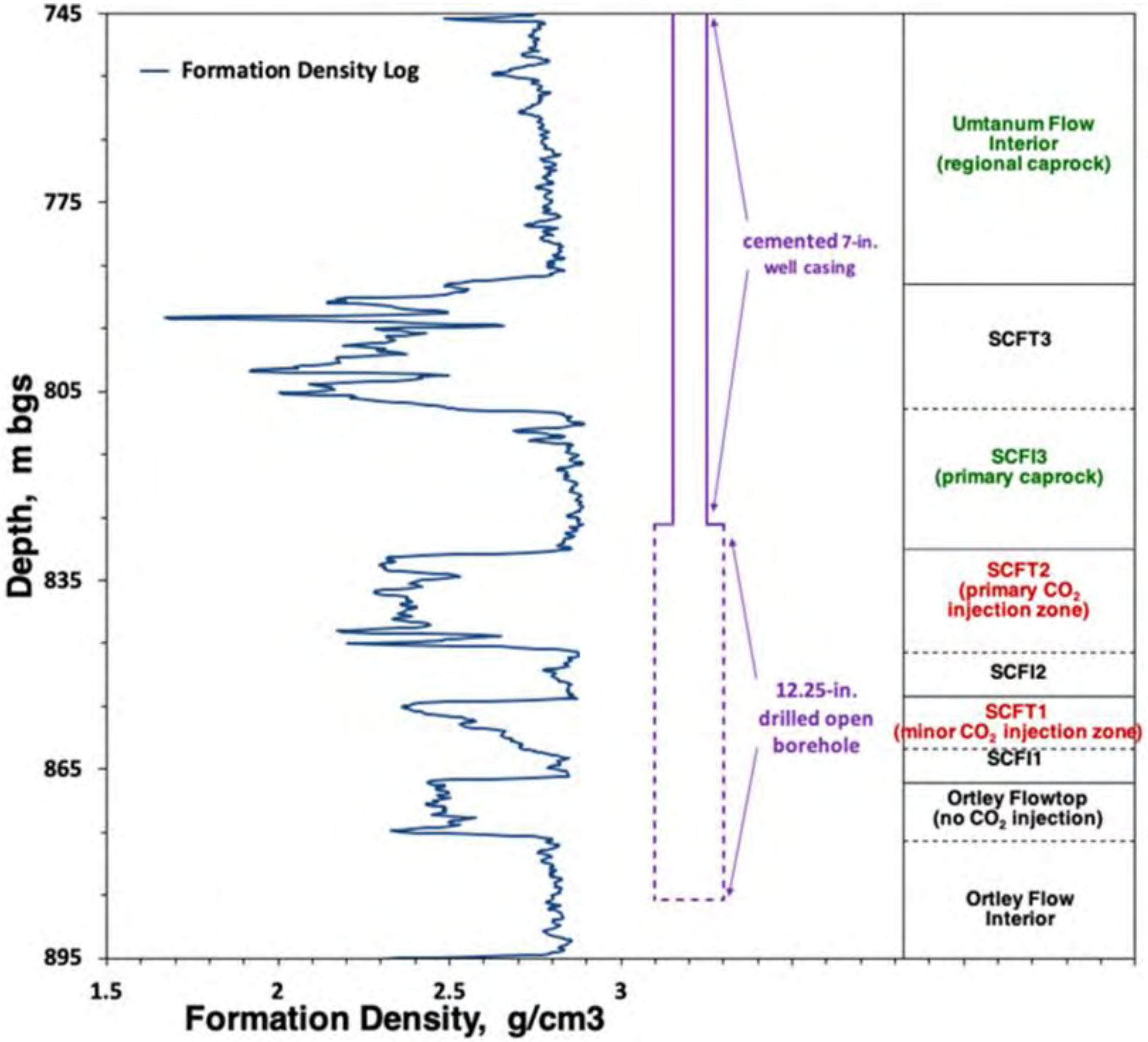
Change in mineral mass (total moles in model domain, negative value indicates dissolution, positive value indicates precipitation) after 1000 MT of CO2 Injection into the Slack Canyon #2 Flow Top.

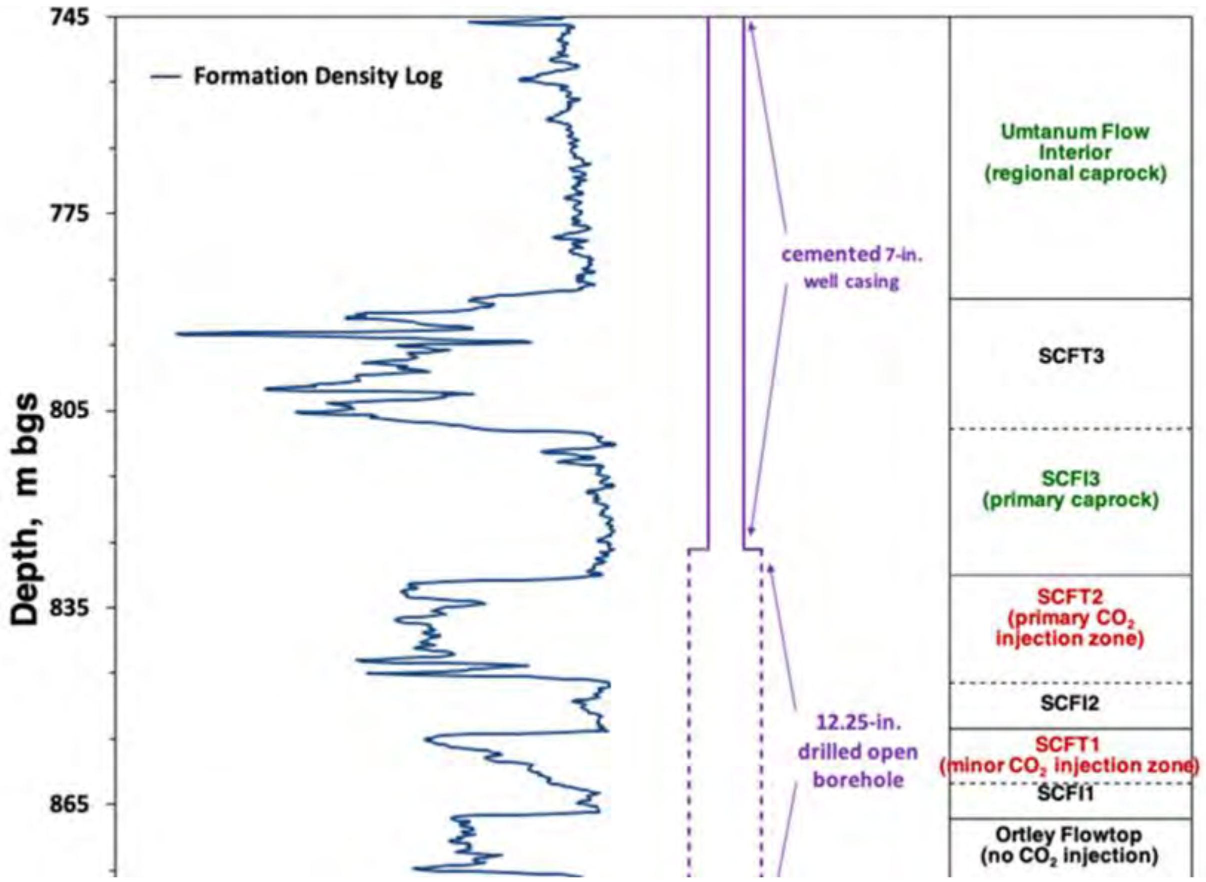
Preliminary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)



Mass balance of 1000 MT of CO2 Injection into the Slack Canyon #2 Flow Top.

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)





Formation density/wireline geophysical log representation of the CRB stratigraphy and injection zone(s) (left) and the resulting conceptual reservoir model (right) used in the numerical simulations. Identified units are UFI, Umtanum Flow Interior; SCFT, Slack Canyon Flow Top; SCFI, Slack Canyon Flow Interior; OFT, Ortley Flow Top; and OFI, Ortley Flow Interior.

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

Environmental Science & Technology

pubs.acs.org/est Article

Quantification of CO_2 Mineralization at the Wallula Basalt Pilot Project

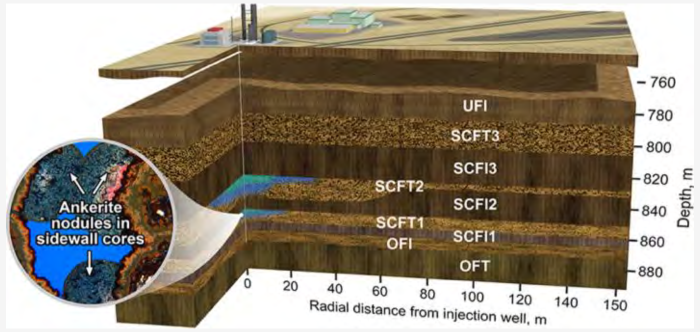
Signe K. White,* Frank A. Spane, H. Todd Schaef, Quin R. S. Miller, Mark D. White, Jake A. Horner, and B. Peter McGrail

Cite This: *Environ. Sci. Technol.* 2020, 54, 14609–14616

Read Online

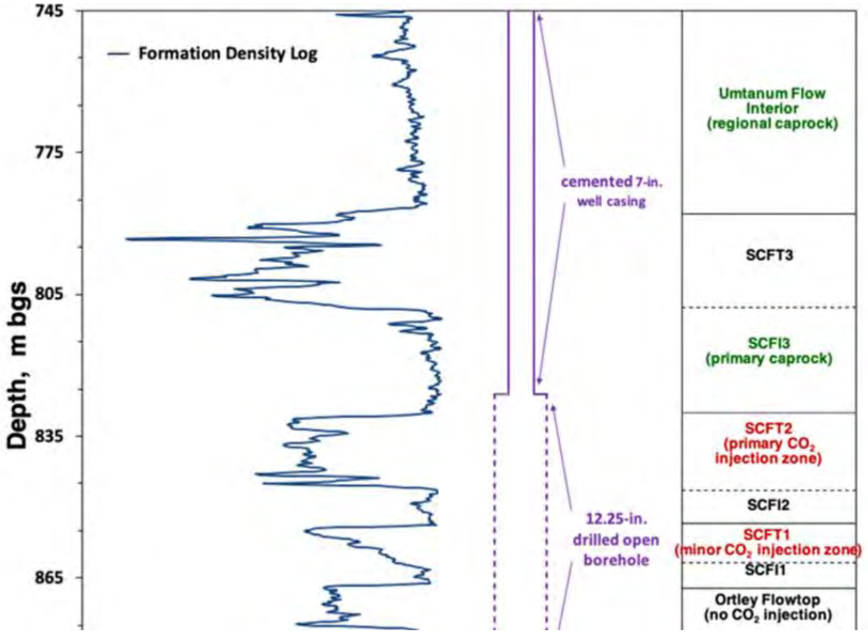
ACCESS | Metrics & More | Article Recommendations | Supporting Information

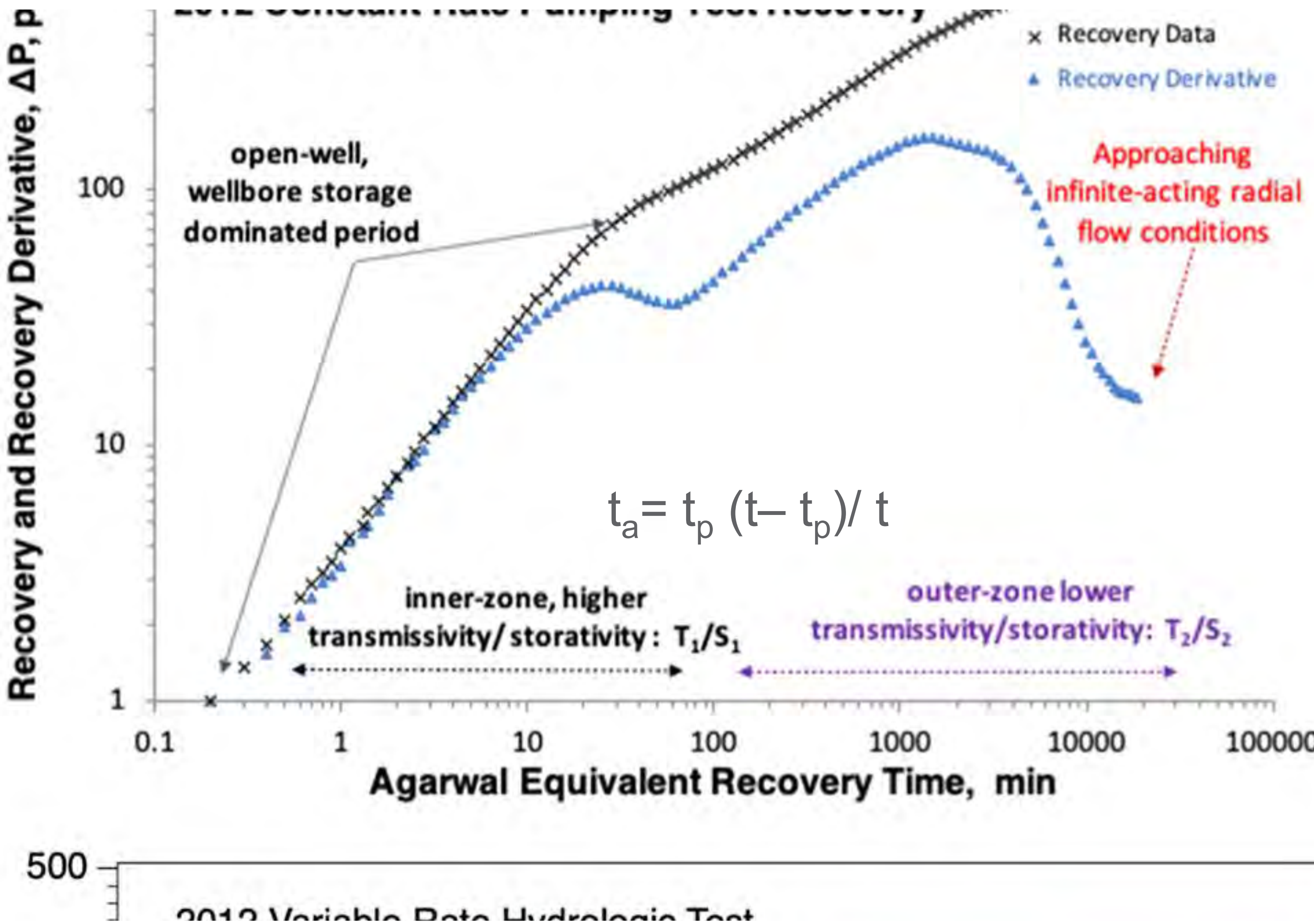
ABSTRACT: In 2013, the Pacific Northwest National Laboratory led a geologic carbon sequestration field demonstration where ~1000 tonnes of CO_2 was injected into several deep Columbia River Basalt zones near Wallula, Washington. Rock core samples extracted from the injection zone two years after CO_2 injection revealed nascent carbonate mineralization that was qualitatively consistent with expectations from laboratory experiments and reactive transport modeling. Here, we report on a new detailed analysis of the 2012 pre-injection and 2015 post-injection hydrologic tests that capitalizes on the difference in fluid properties between $scCO_2$ and water to assess changes in near-field, wellbore, and reservoir conditions that are apparent approximately two years following the end of injection. This comparative hydrologic test analysis method provides a new way to quantify the amount of injected CO_2 that was mineralized in the field test. Modeling results indicate that approximately 60% of the injected CO_2 was sequestered via mineralization within two years, with the resulting carbonates occupying ~4% of the available reservoir pore space. The method presented here provides a new monitoring tool to assess the fate of CO_2 injected into chemically reactive basalt formations but could also be adapted for long-term monitoring and verification within more traditional subsurface carbon storage reservoirs.



Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- Pre-injection hydrologic test (2012)
- Three brecciated interflow zones
- 21-day extended hydrologic tests
- Constant-rate pumping to 425 m drawdown
- Variable-rate pumping to hold drawdown at 425 m
- Identification of two distinct flow-regime/boundary conditions present within the SCFT2 basalt layer





Pre-CO2 injection diagnostic test analysis, indicating a higher transmissivity/storativity inner zone surrounding the Wallula Pilot well.

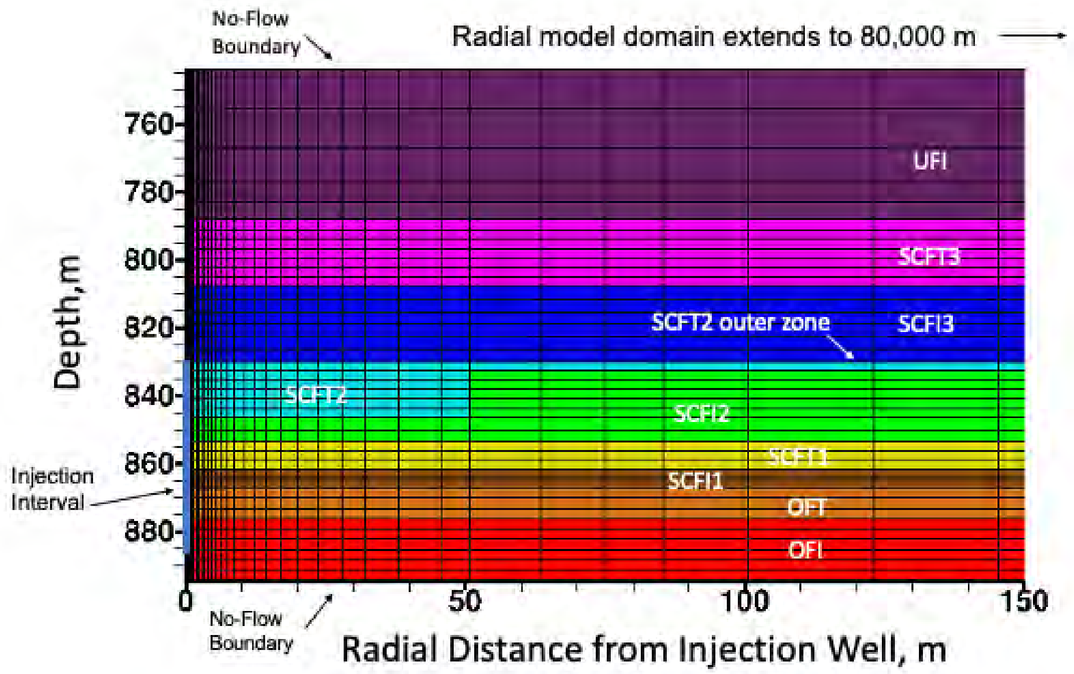
Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- Pre-injection hydrologic test (2012)
- Modeling via cylindrical grid (STOMP-W)

Table S1. Hydraulic Properties (porosity, permeability, and transmissivity) of individual basalt layers

Interval Abbreviation	Figure 1 Interval Color Reference	Interval Description	Depth to Top (m)	Depth to Bottom (m)	Thickness (m)	Porosity† (%)	Permeability † (mD)	Transmissivity (m^2/day)
UFI	purple	Umtanum flow interior (UFI, secondary caprock)	743.7	787.9	44.2	1	2.63E-10	1.35E-11
SCFT3	pink	Slack Canyon #3 flow top (SCFT3) porosity zone (no injection)	787.9	807.7	19.8	25	1.41E+02	3.25E+00
SCFI3	blue	Slack Canyon #3 flow interior (SCFI3, primary caprock)	807.7	830.0	22.3	1	2.63E-10	6.78E-12
SCFT2	cyan	Slack Canyon #2 flow top porosity zone (SCFT2 Inner, first 50 m)	830.0	846.4	16.4	22	8.28E+01	1.58E+00
SCFT2	cyan	Slack Canyon #2 flow top (SCFT2 Outer)	830.0	832.7	2.7	1	4.20E+01	1.33E-01
SCFI2	green	Slack Canyon #2 flow top outer non-contributing, (with properties of SCFI2)	832.7	846.4	13.7	1	2.63E-10	4.18E-12
SCFI2	green	Slack Canyon #2 flow interior (SCFI2, seal)	846.4	853.4	7.0	1	2.63E-10	2.14E-12
SCFT1	yellow	Slack Canyon #1 flow top (SCFT1) porosity zone (injection)	853.4	861.7	8.3	13	4.67E+00	4.46E-12
SCFI1	brown	Slack Canyon #1 flow interior (SCFI1, seal)	861.7	867.1	5.4	1	2.63E-10	1.67E-12
OFT	maroon	Ortley flow top (OFT, no injection)	867.1	876.3	9.2	1	2.63E-10	2.79E-12
OFI	red	Ortley flow interior (OFI, lower confining zone)	876.3	894.6	18.3	1	2.63E-10	5.57E-12

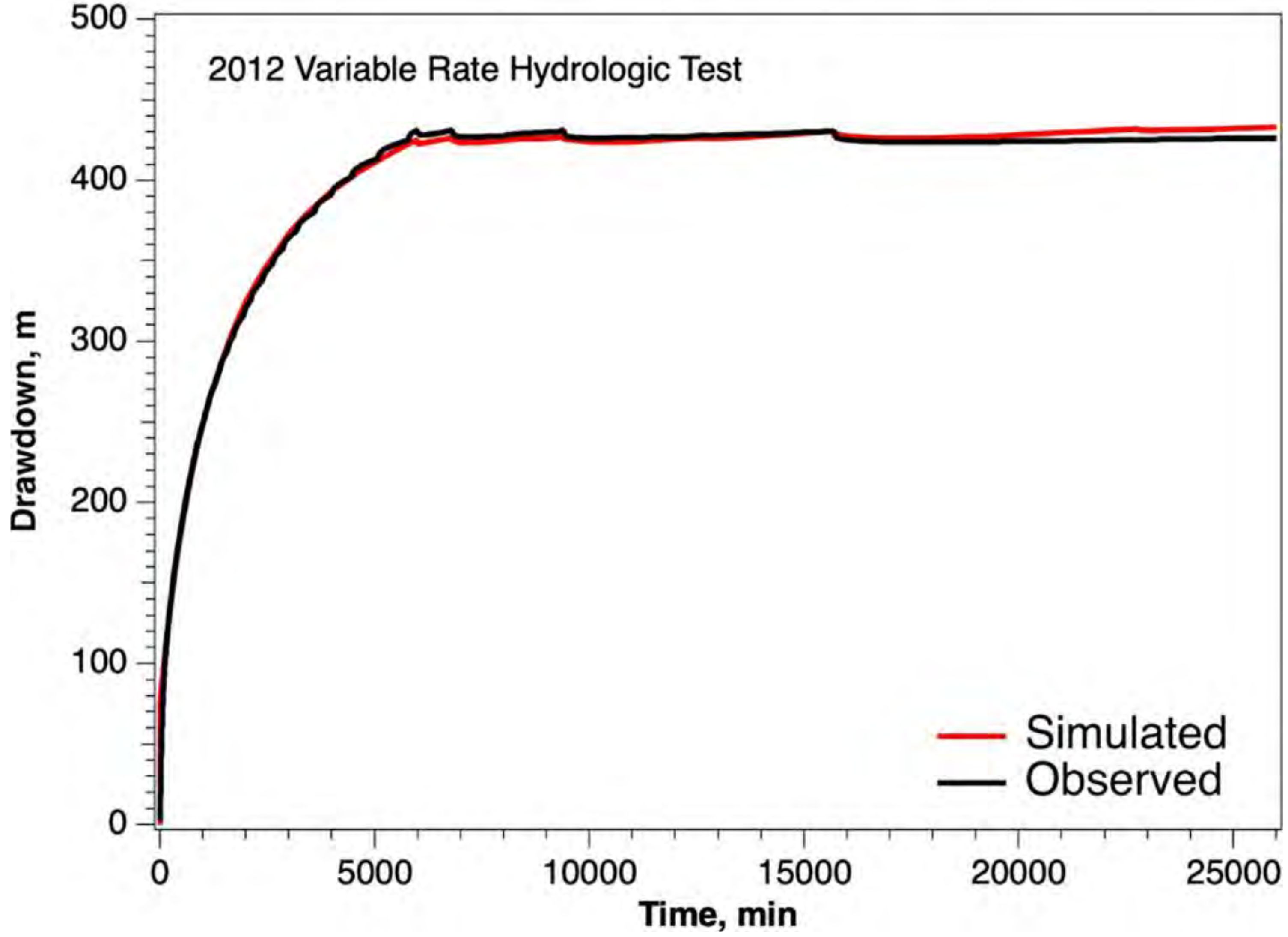
† Porosity and permeability of 1% and 2.63E-10 mD assigned to flow interiors (shaded values) based on Spane et al.[1] and Eslinger[2]. These same parameters were used for the Ortley flow top (OFT) and the outer Slack Canyon #2 flow top (SCFT2) non-contributing pinched zone based on the low storativities revealed from hydrologic and CO_2 injection test results.

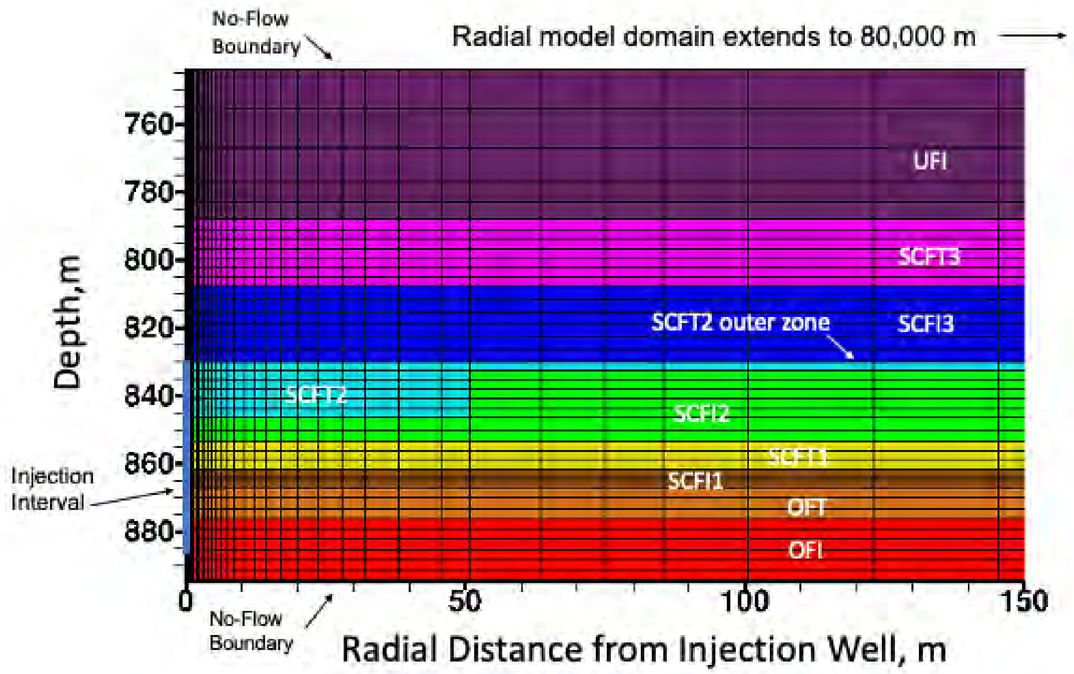


Numerical model implementation showing grid, model layers (basalt units), injection interval and boundary conditions.

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- Pre-injection hydrologic test (2012)
- Modeling via cylindrical grid (STOMP-W)



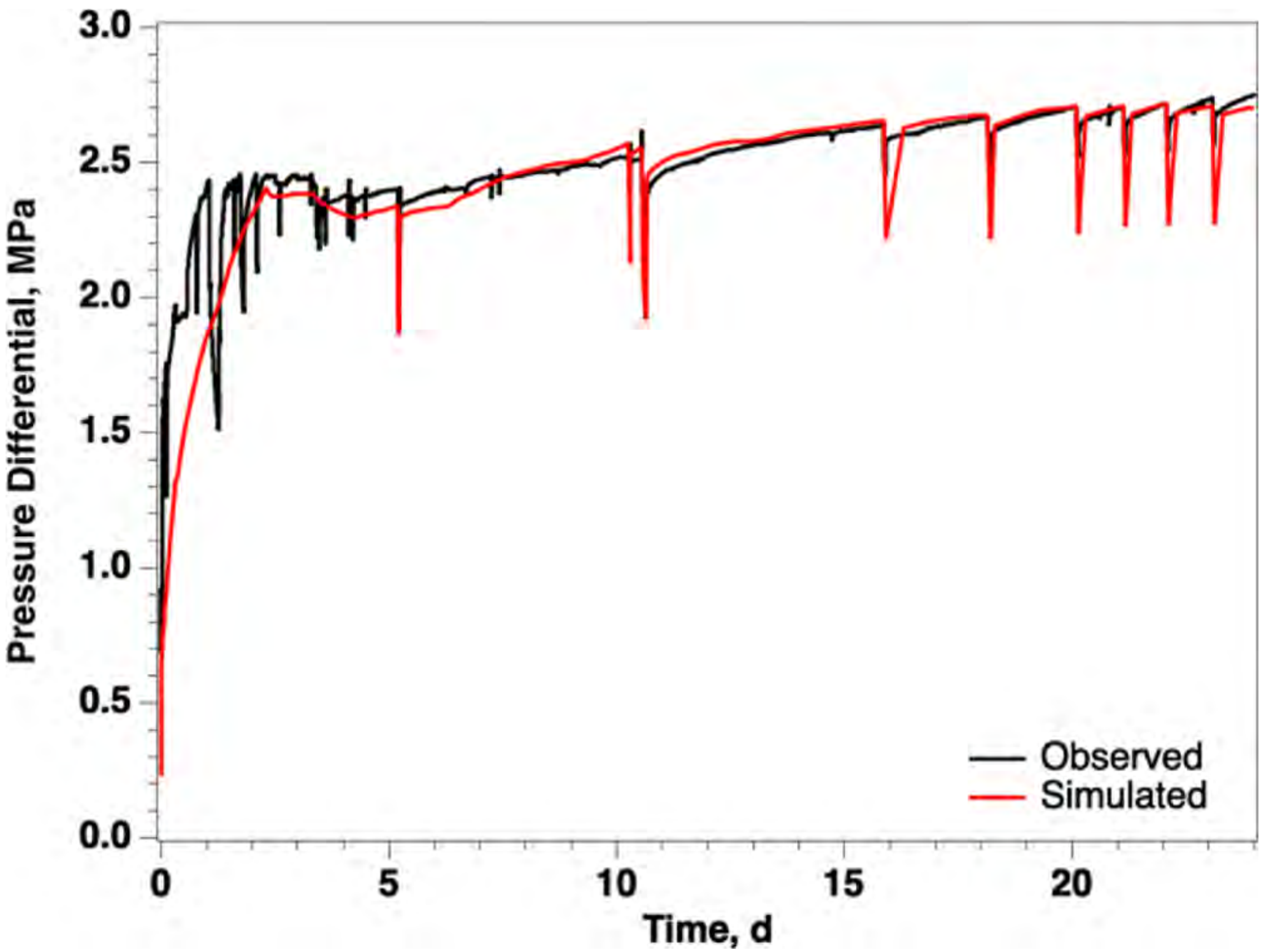


Numerical model implementation showing grid, model layers (basalt units), injection interval and boundary conditions.

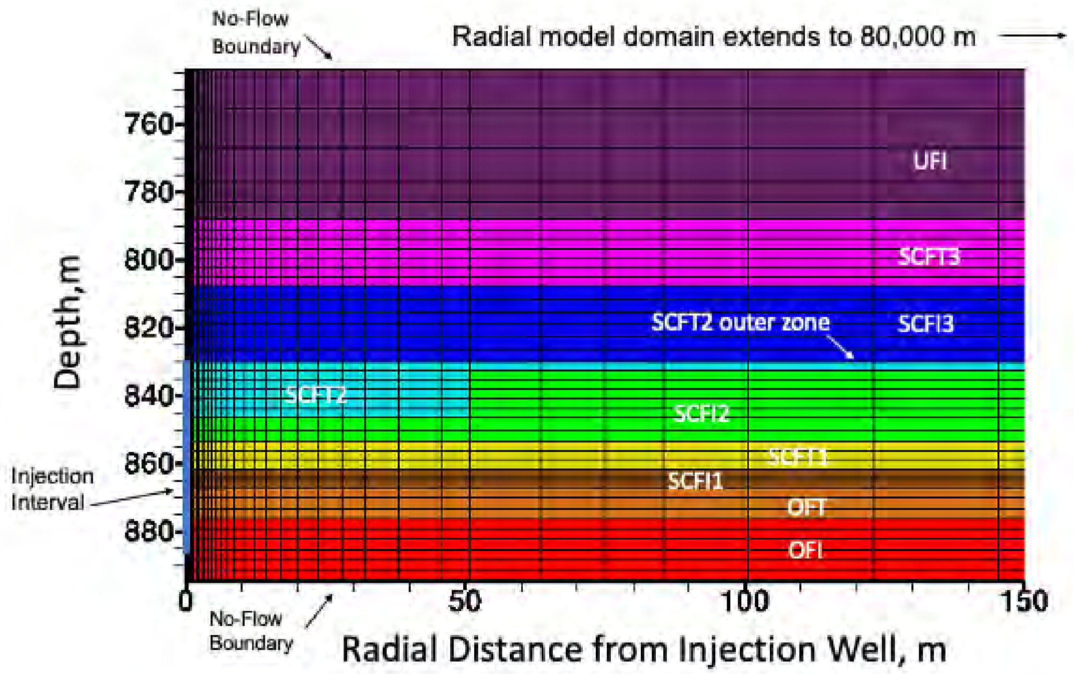
Final numerical model calibration results based on the 2012 variable rate hydrologic test.

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- CO_2 injection (2013)
- Modeling via cylindrical grid (STOMP-CO2)



Injection pressure response during the August 2013 CO2 injection (black) and the modeled response (red) obtained with our calibrated STOMP-CO2 reservoir model.

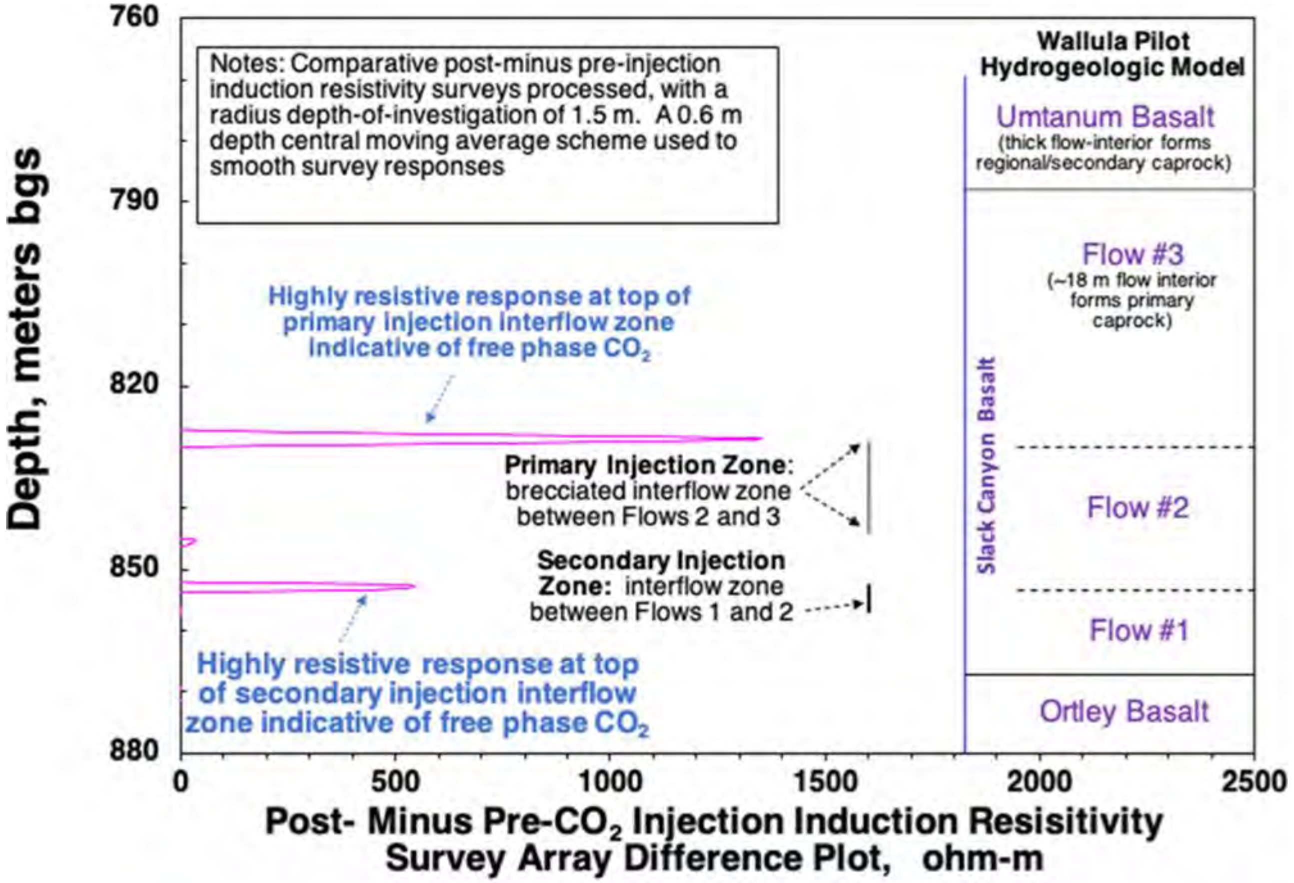


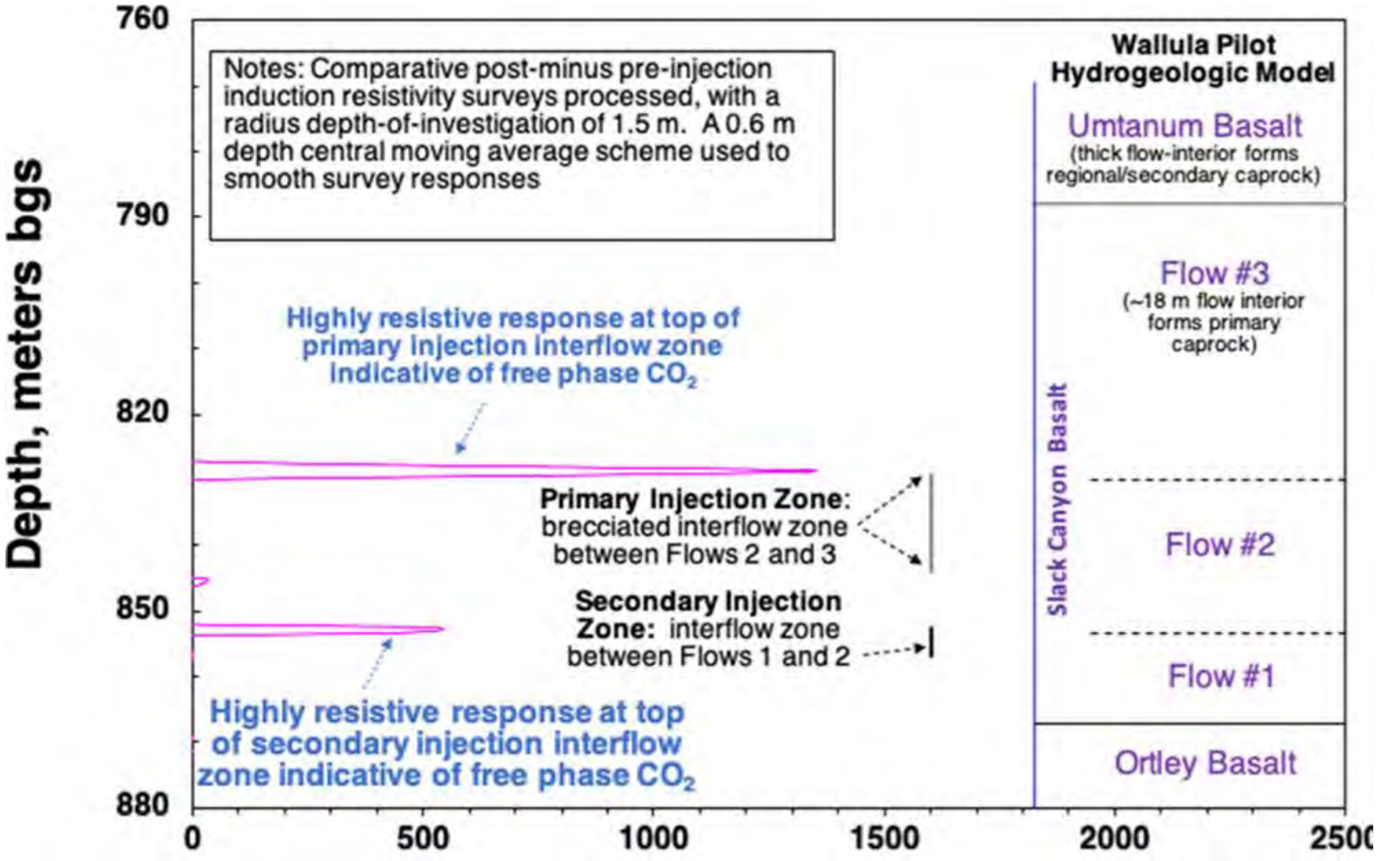
Numerical model implementation showing grid, model layers (basalt units), injection interval and boundary conditions.

Pacific Northwest NATIONAL LABORATORY

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- CO_2 post-injection geophysical survey (2015)
- Modeling via cylindrical grid (STOMP-CO2)

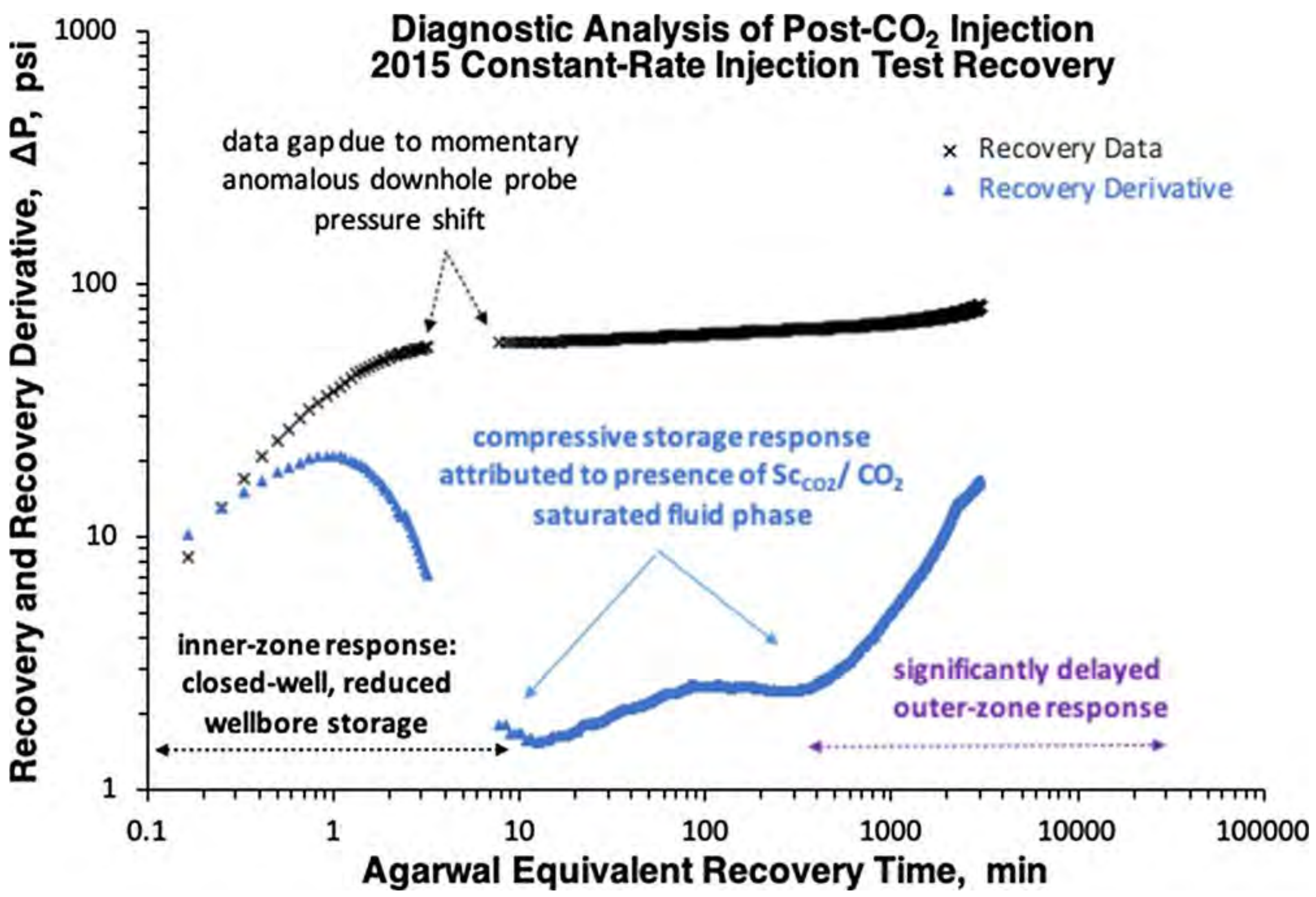




Post- minus pre-CO2 injection induction resistivity survey array difference plot showing the presence of highly resistive free-phase CO2 in the top two injection zone reservoirs (left) and simulated CO2 gas saturations showing a similar distribution (right).

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

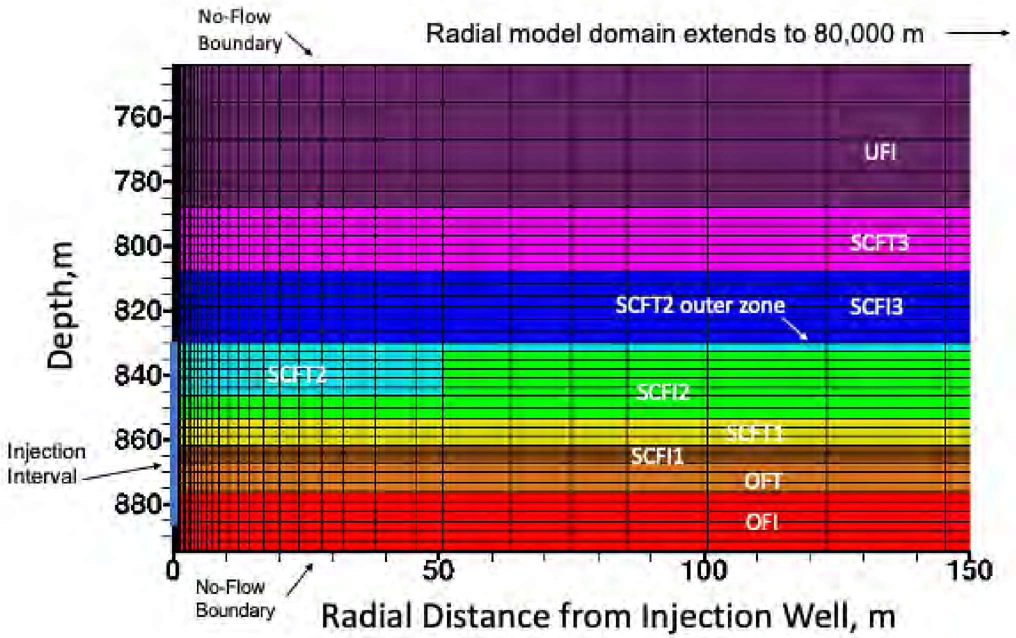
- Post-injection hydrologic test (2015)
- No discernible near- to intermediate-scale changes in reservoir hydraulic property conditions were observed for either the post-injection pressurized-slug/pulse testing and/or in the injection/recovery test analysis results.
- Analysis of the injection/recovery response identified the presence of a highly compressible intervening fluid zone located between the inner and outer formational reservoir regions surrounding the well.



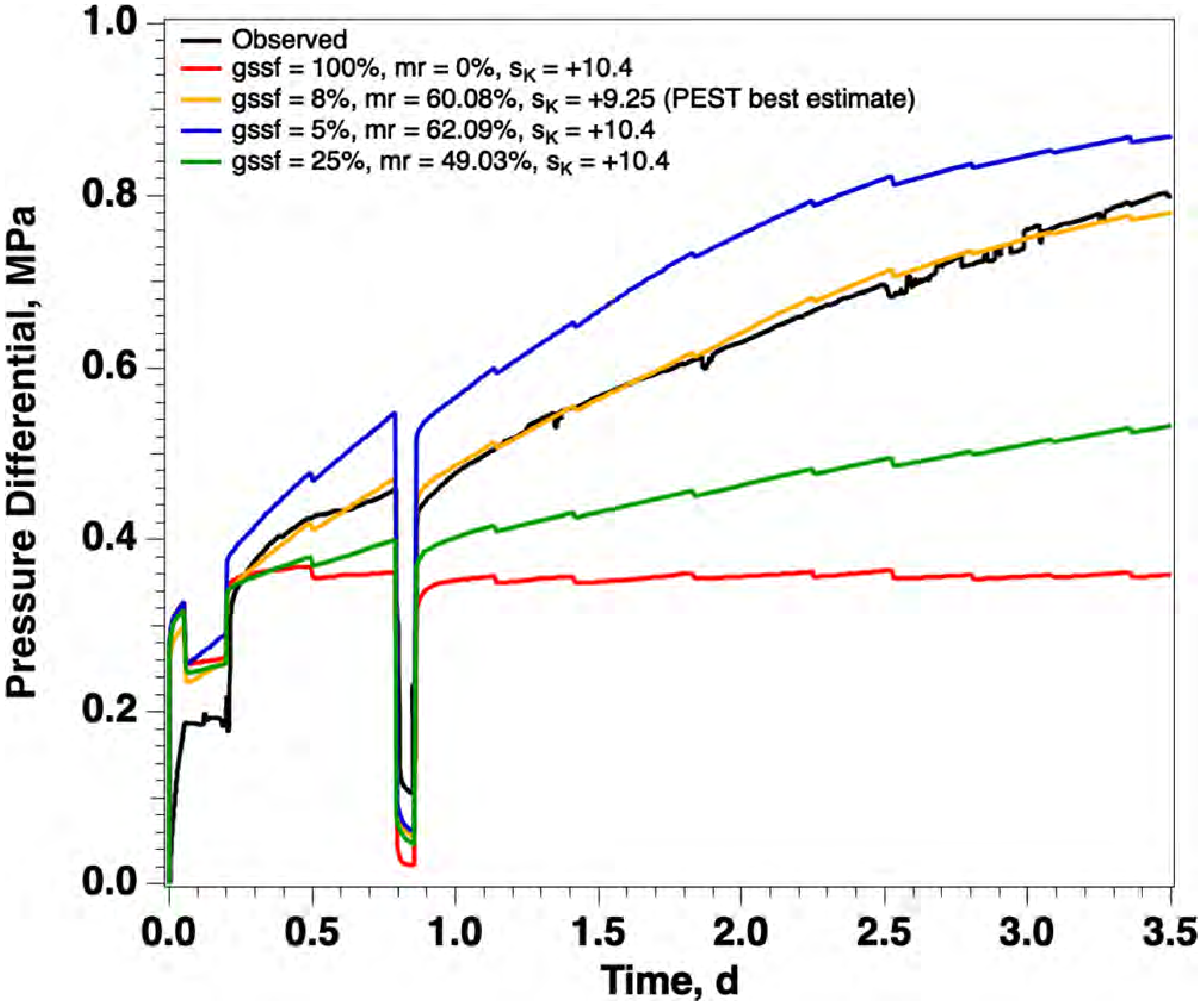
Post-CO2 injection diagnostic test analysis indicating the presence of a compressive storage fluid phase within the injection reservoir.

Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- Post-injection hydrologic test (2015)
- Modeling via cylindrical grid (STOMP-CO2)

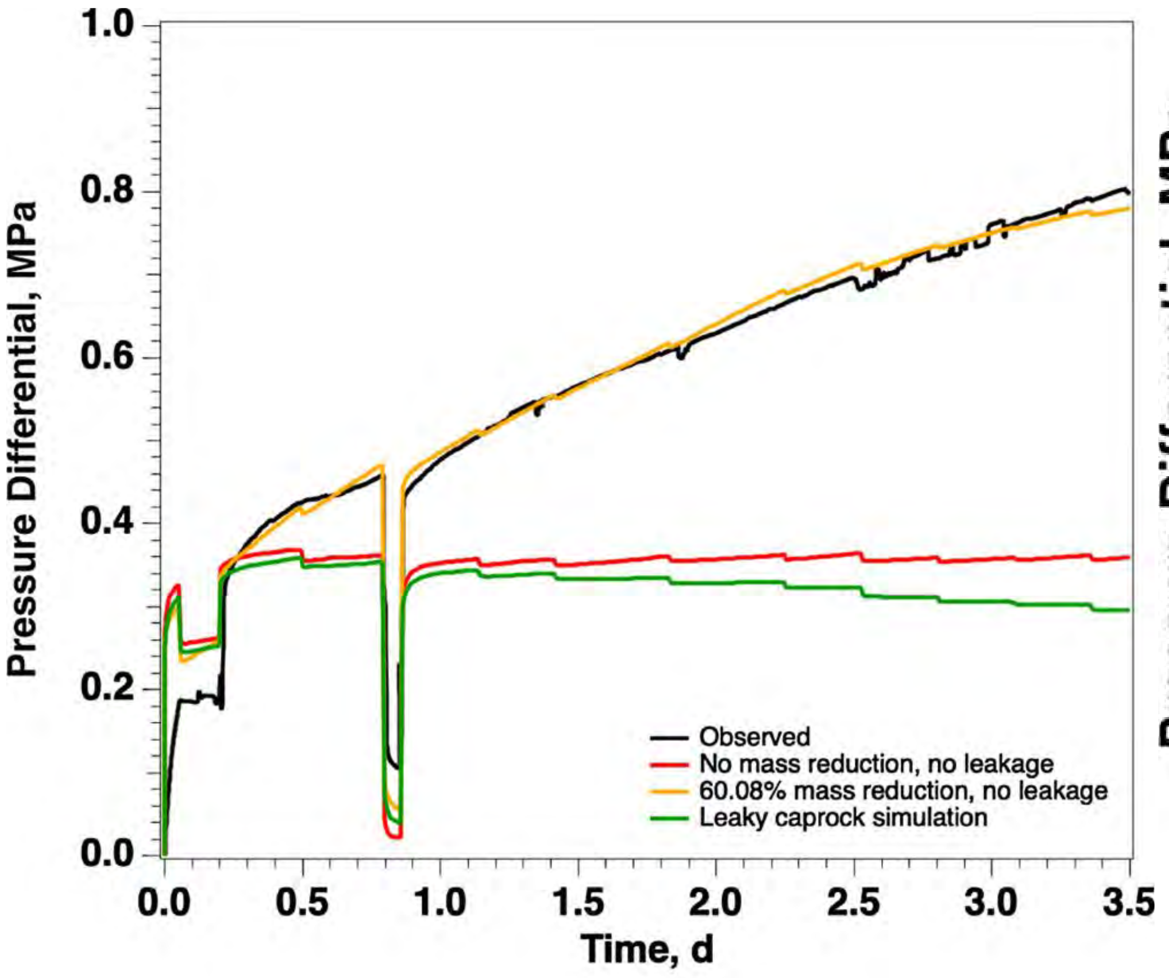


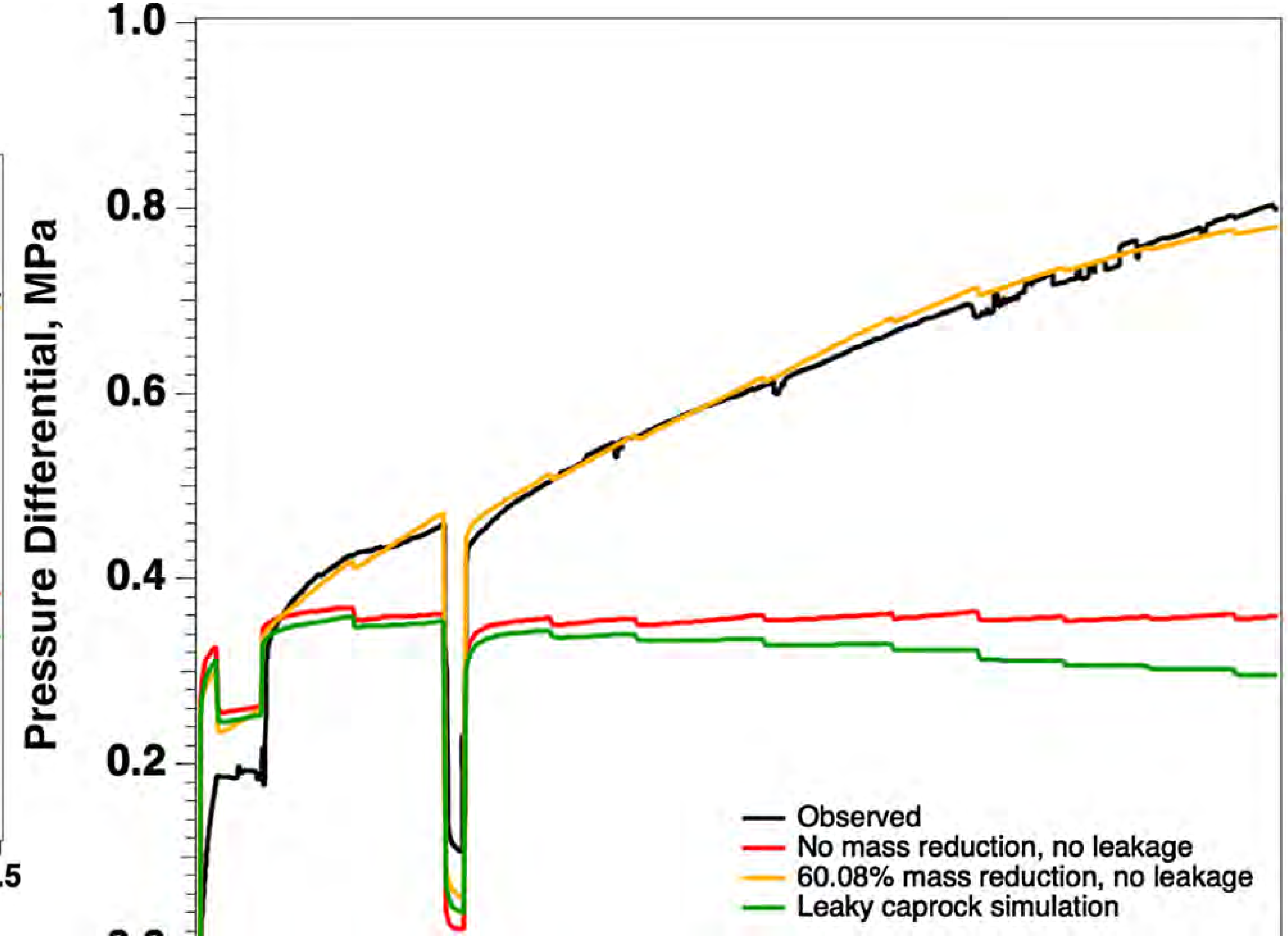
2015 Post-injection hydrologic test simulation results showing the observed pressure response in the injection well against the simulated pressure response with varying well skin factors (s_K) and gas saturation scaling factors (gssf) with associated CO2 mass reduction percentages (mr).



Quantification of CO_2 Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

- Post-injection hydrologic test (2015)
- Modeling via cylindrical grid (STOMP-CO2)





Comparison of leaky caprock simulation pressure response to observed pressure response during the 2015 post-injection hydrologic test (left) and during CO2 injection (right).

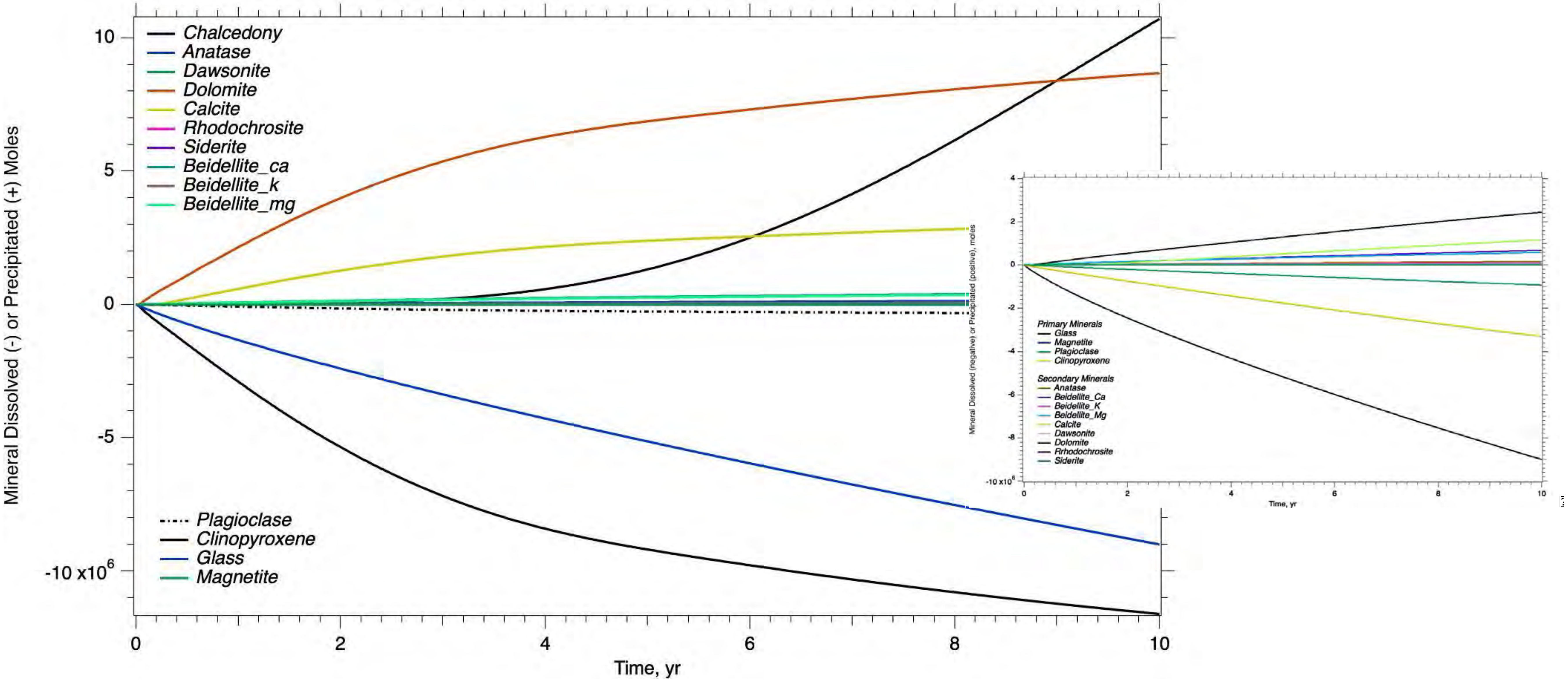
Secondary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

Reaction	log K_{eq}	k_{ref} at T_{ref}, mol m^{-2} s^{-1}	T_{ref}, °C	E_a, kJ mol^{-1}	h
Plagioclase + 6.186H^+ = 1.5465Al^{3+} + 0.4535Na^+ + 3.093H_2O + 2.4535SiO_2 + 0.5465Ca^{++}	15.29	8.03×10^{-08}	60	42.1	0.626
Clinopyroxene + 4H^+ = Ca^{2+} + 0.25Fe^{2+} + 0.75Mg^{2+} + 2H_2O + 2SiO_2(aq)	19.89	4.13×10^{-05}	60	78.0	0.700
Glass + 0.8869H^+ = 0.429H_2O + 0.2051Al^{3+} + 0.0378Ca^{2+} + 0.0364Fe^{2+} + 0.0329K^+ + 0.0049Mg^{2+} + 0.0056Mn^{2+} + 0.0693Na^+ + SiO_2(aq) + 0.007Ti(OH)4(aq)	-2.60	3.93×10^{-08}	100	30.3	0.318
Magnetite + 6H^+ = 3Fe^{2+} + 0.5O_2(g) + 3H_2O	-5.15	8.34×10^{-11}	60	18.6	0.279

Reaction	log K_{eq}	k_{ref} at T_{ref}, mol m^{-2} s^{-1}	T_{ref}, °C	E_a, kJ mol^{-1}	h
Anatase + 2H_2O = $Ti(OH)_4$(aq)	9.65	4.47×10^{-09}	25	37.9	0.421
Beidellite-Ca + 7.32H^+ = 0.165Ca^{2+} + 2.33Al^{3+} + 3.67SiO_2(aq)	4.65	1.05×10^{-11}	25	23.6	0.340
Beidellite-K + 7.32H^+ = 0.33K^+ + 2.33Al^{3+} + 3.67SiO_2(aq)	4.43	1.05×10^{-11}	25	23.6	0.340
Beidellite-Mg + 7.32H^+ = 0.165Mg^{2+} + 2.33Al^{3+} + 3.67SiO_2(aq)	4.60	1.05×10^{-11}	25	23.6	0.340
Calcite + H^+ = Ca^{2+} + HCO_3^-	1.70	5.01×10^{-01}	25	14.4	1.000
Chalcedony = SiO_2(aq)	-3.56	5.89×10^{-13}	25	74.5	0.000
Dawsonite + 3H^+ = Al^{3+} + Na^+ + HCO_3^-	3.91	1.00×10^{-07}	25	62.8	0.000
Magnesite + H^+ = Mg^{++} + HCO_3^-	2.04	4.17×10^{-07}	25	14.4	1.000
Rhodochrosite + H^+ = HCO_3^- + Mn^{2+}	-0.32	1.02×10^{-03}	25	21.0	0.900
Siderite + H^+ = Fe^{2+} + HCO_3^-	-0.38	1.02×10^{-03}	25	21.0	0.900

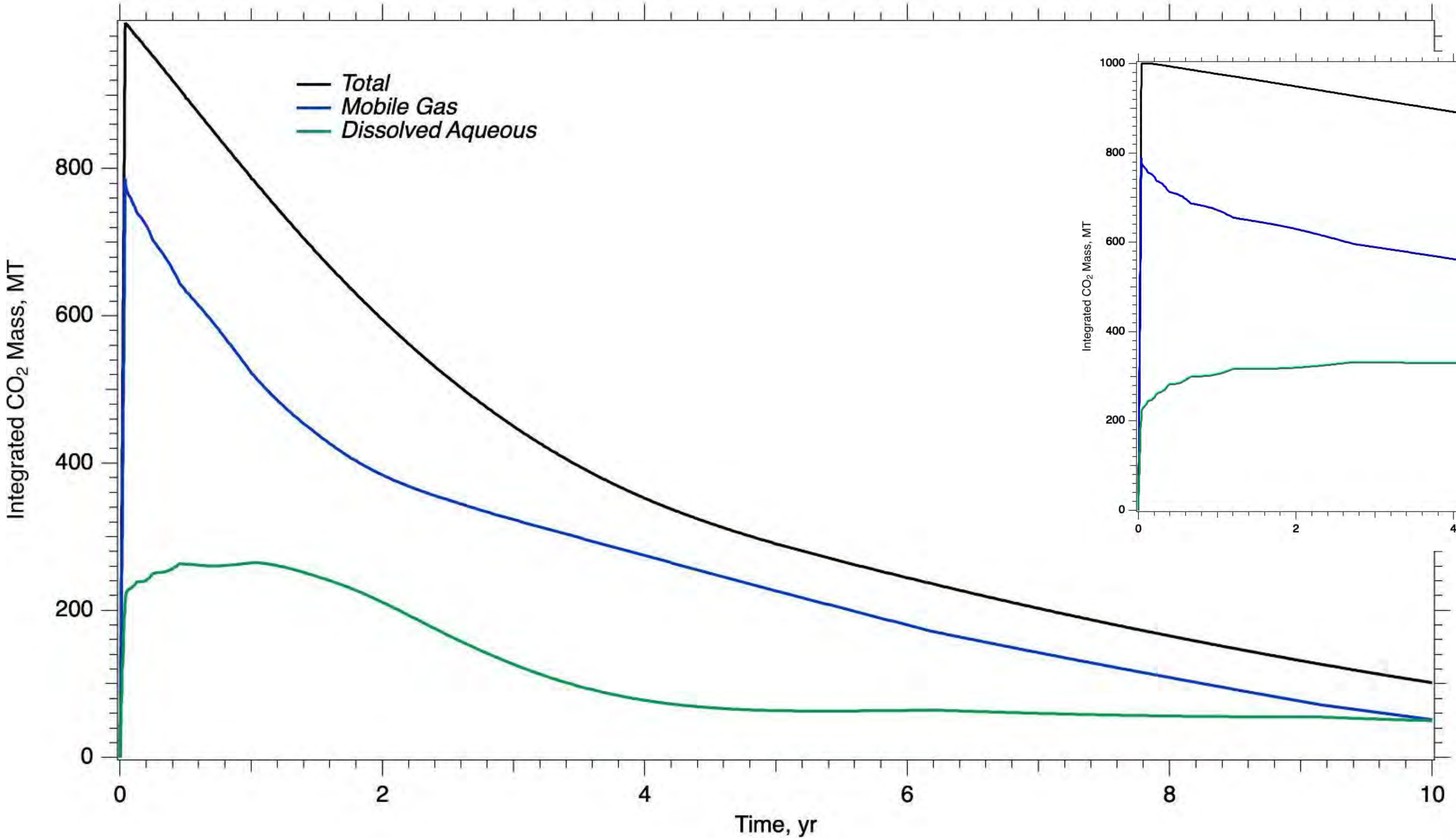
$$r = k_{ref}\, A \exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right]\left(1-\frac{Q}{K_{eq}}\right)10^{(-h\, pH)}$$

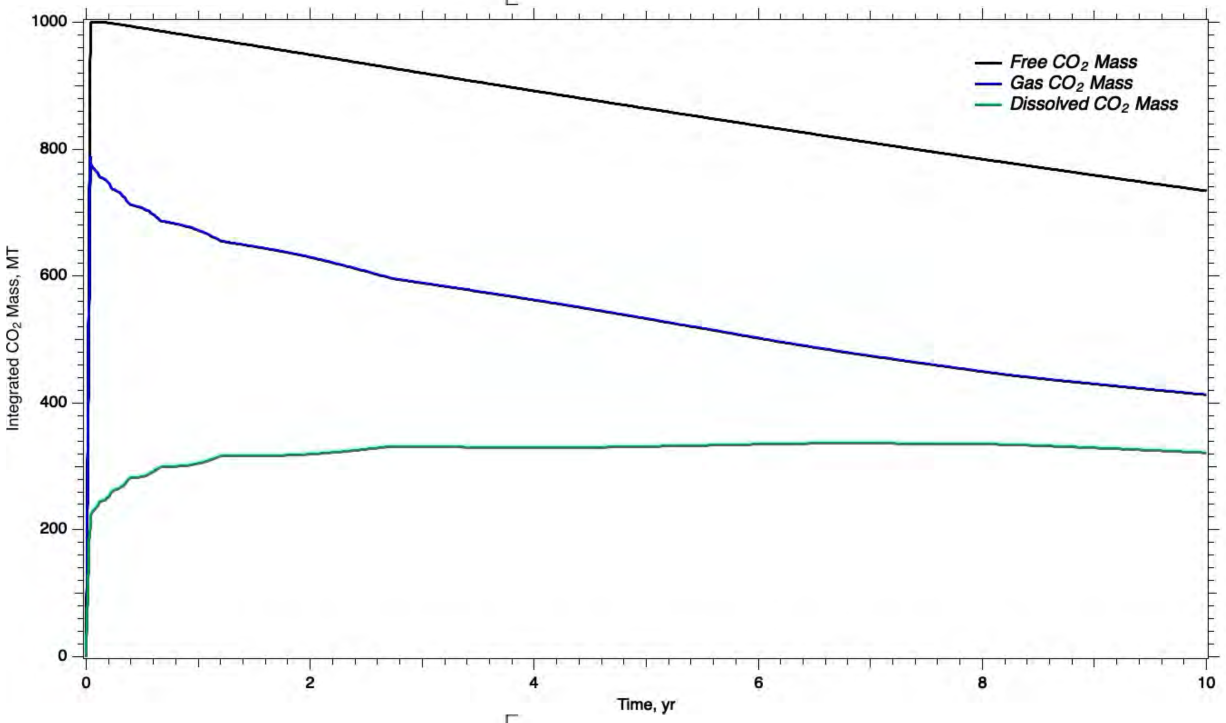
Secondary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)



Change in mineral mass (total moles in model domain, negative value indicates dissolution, positive value indicates precipitation) after 1000 MT of CO2 Injection into the Slack Canyon #2 Flow Top.

Secondary Modeling of Mineralization
Wallula Basalt Pilot Project Injection (1000 tonnes)

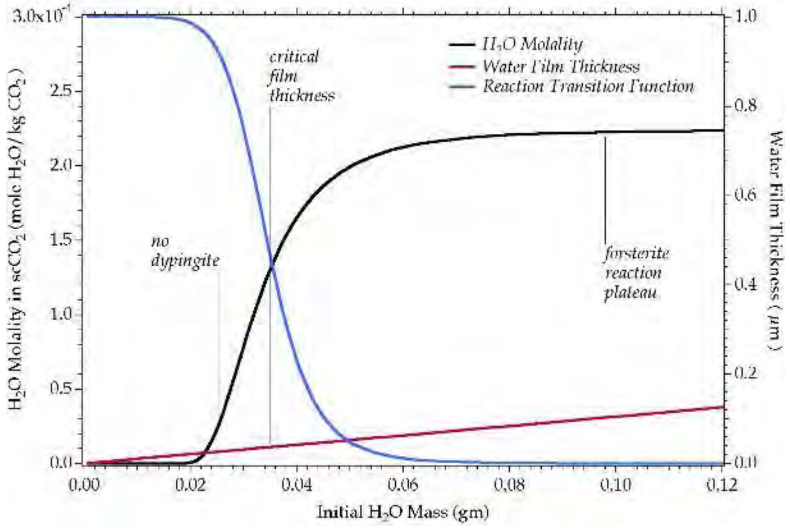




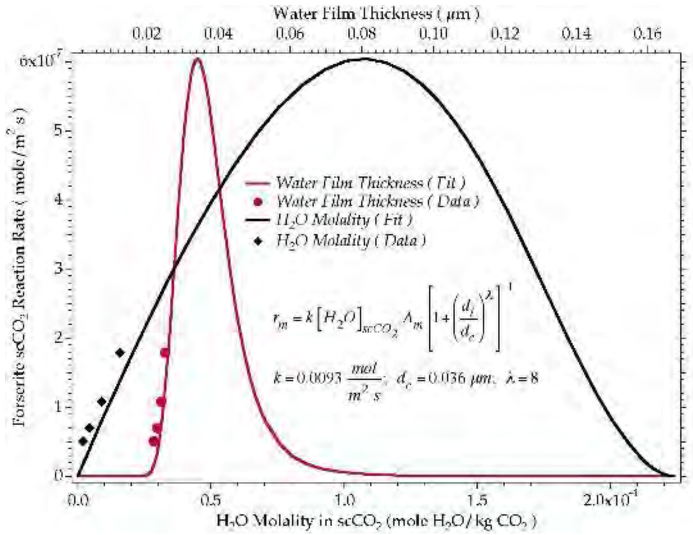
Mass balance of 1000 MT of CO2 Injection into the Slack Canyon #2 Flow Top.

Model for Reaction Mechanism Transitions
Laboratory Experiments at PNNL

Reaction Transition



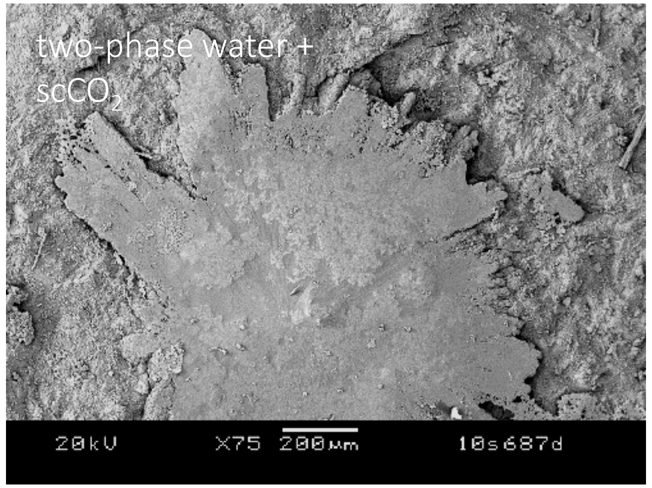
Forsterite Kinetics

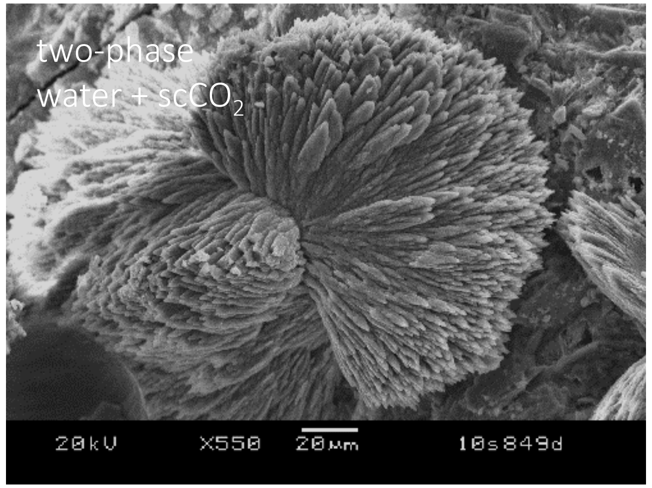


Dissolution-Precipitation

$$r_m = -\mathrm{sgn}\left[\log\left(\frac{Q_m}{K_m}\right)\right] k_{25} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]$$

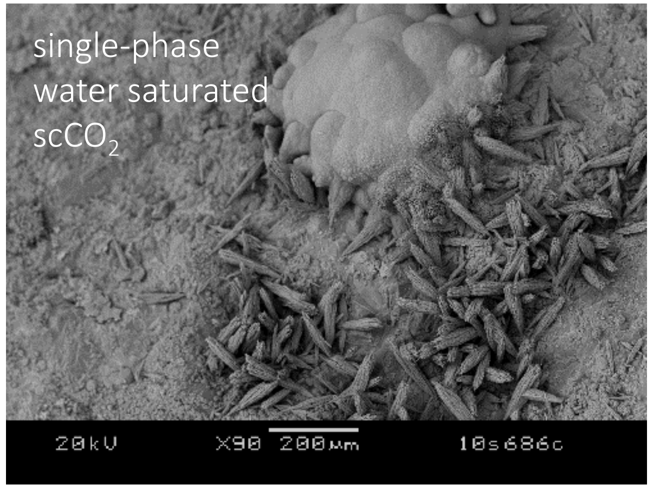
$$A_m \left|\left(\frac{Q_m}{K_m}\right)^m - 1\right|^n \left\{\left(\frac{d_l}{d_c}\right)^\lambda \left[1+\left(\frac{d_l}{d_c}\right)^\lambda\right]^{-1}\right\}$$





Sequential Transformation

$$r_m = k\left[H_2O\right]_{scCO_2} A_m \left[1+\left(\frac{d_l}{d_c}\right)^\lambda\right]^{-1}$$



Early Career Contributions Driving Basalt Carbon Storage Advances

U.S. DEPARTMENT OF ENERGY

Pacific Northwest NATIONAL LABORATORY

- Outreach is a keystone of our program, PUIs to R1s
- Early career researchers include interns, postdocs, staff, visitors, etc
- Product-driven research experience cultivates and unleashes talent
- Diversity and inclusion enables innovation and creativity, breadth of perspectives needed for global challenges
- DOE synergy: FECM (MLEF), SC (VFP, SULI, SCGSR), NNSA (MSIIP)


Ellen Polites (MLEF)


Jade Holliman (MSIPP)


Charles Depp (SULI)


Dr. Sandy Taylor


Dr. Anil Battu


Dr. Nabajit Lahiri


Dr. Ross Cao (CUSP)


Prof. Briana Aguila (VFP)


Landon Hardee (VFP)

FISK UNIVERSITY 1866

UNIVERSITY OF PITTSBURGH

WHITMAN COLLEGE

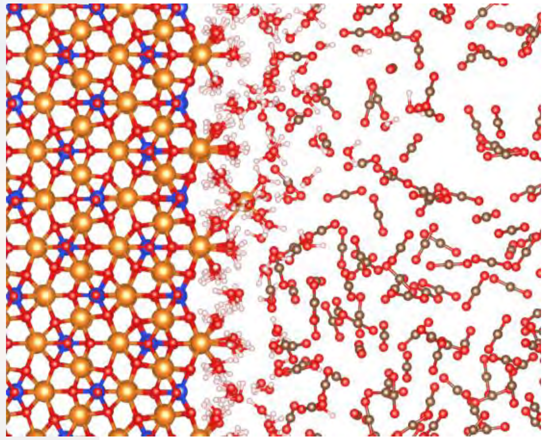
FRANCIS MARION UNIVERSITY 1970

UNIVERSITY OF WYOMING

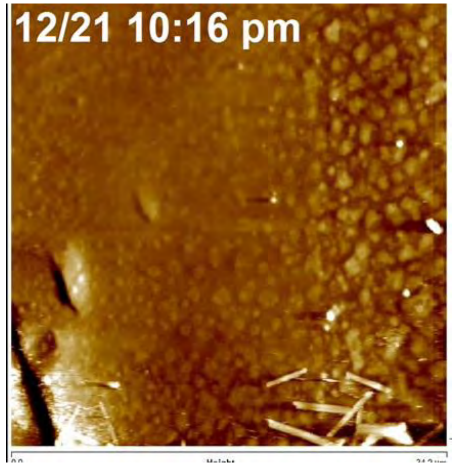
OSU

Multiscale Approach Enables Commercial-Scale Deployment Catalyzed by Scientific Discovery

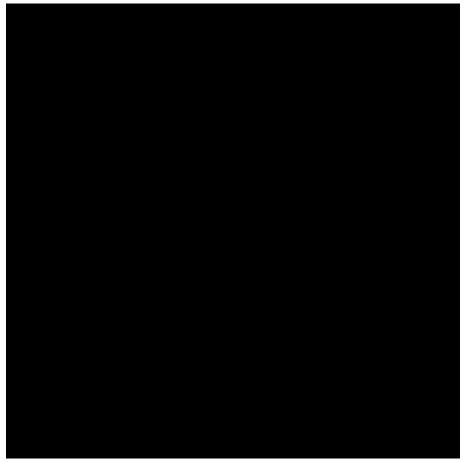
Molecular | Micro | Bench | Systems | Deployment | Vision



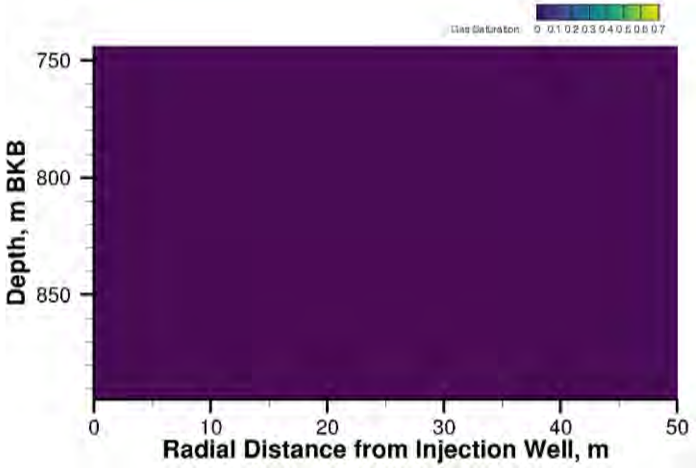
Theory & Simulation



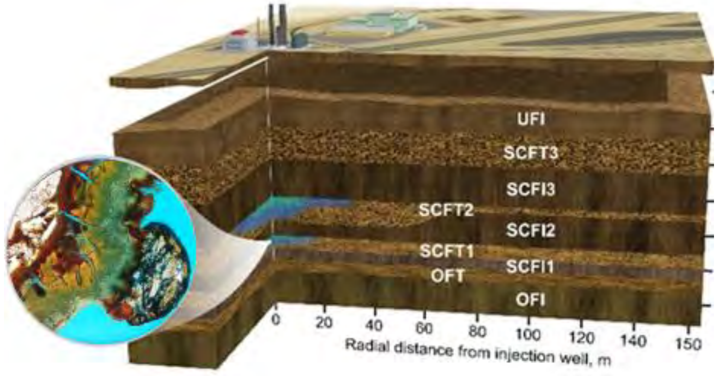
Kinetics & Pathways



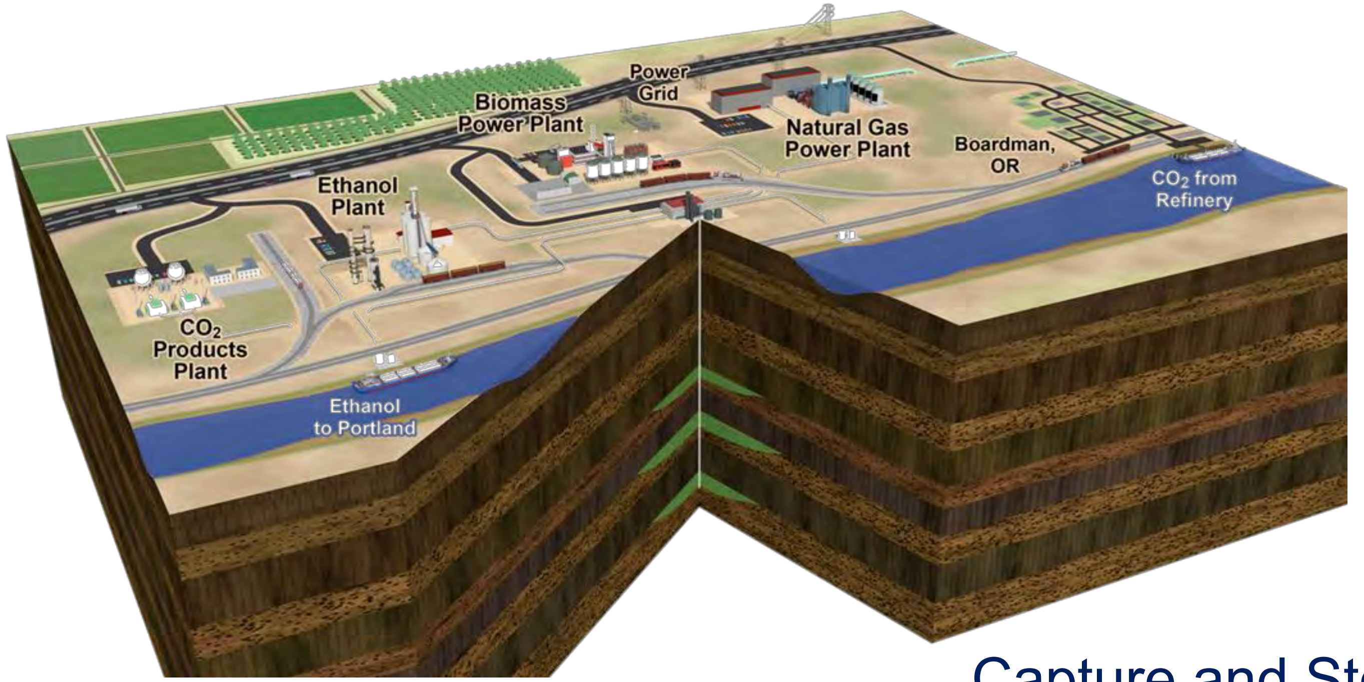
Precipitation in Pores



Reservoir Modelling



Field Demonstration



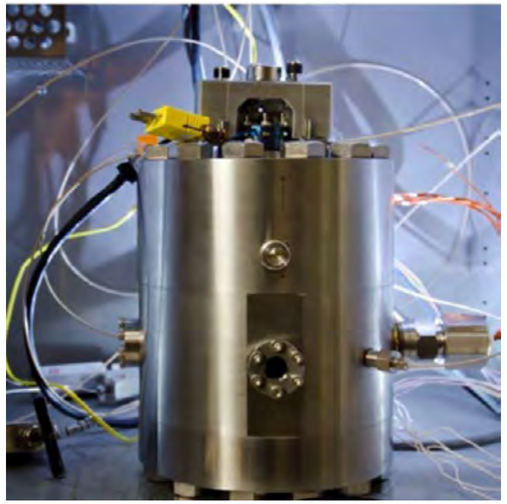
Capture and Storage Hub

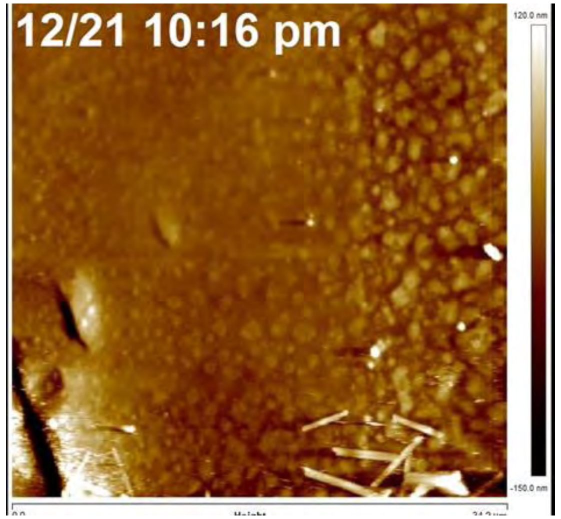
Understanding Wet CO_2 Vital for Predicting and Optimizing Carbon Storage in Mafic-Ultramafic Formations

Pacific Northwest NATIONAL LABORATORY

- PNNL has pioneered the study of wet supercritical CO_2
  - CO_2-H_2O immiscible fluids coexist at GCS conditions
  - Wet $scCO_2$ more reactive than aqueous-dissolved CO_2
  - Anomalous carbonation kinetics, pathways, and mechanisms
  - Field-lab kinetics paradigm flipped on its head
- Unparalleled Insight enabled by suite of high-pressure experimental capabilities
  - AFM, XRD, ATR-FTIR, Raman, QCM, MAS-NMR
  - Experimental results will parameterize reservoir simulators
- High-profile results released in 2022 (IF >43 and >34)

nature materials ARTICLES
https://doi.org/10.1038/s41563-021-01154-5

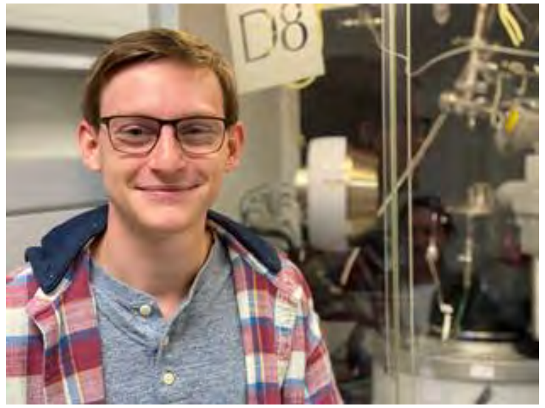




Zhang et al. 2022, *In situ imaging of amorphous intermediates during brucite carbonation in supercritical CO_2*, Nature Materials https://doi.org/10.1038/s41563-021-01154-5

nature reviews chemistry

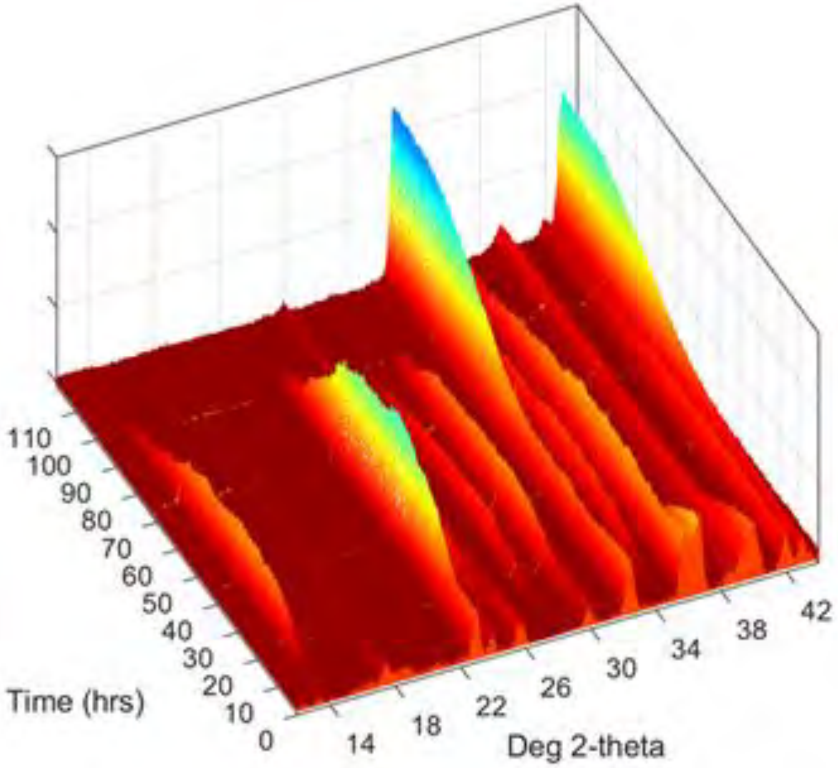
Qomi et al. 2022, *Molecular-Scale Mechanisms of CO_2 Mineralization in Nanoscale Interfacial Water Films*, Accepted at Nature Reviews Chemistry



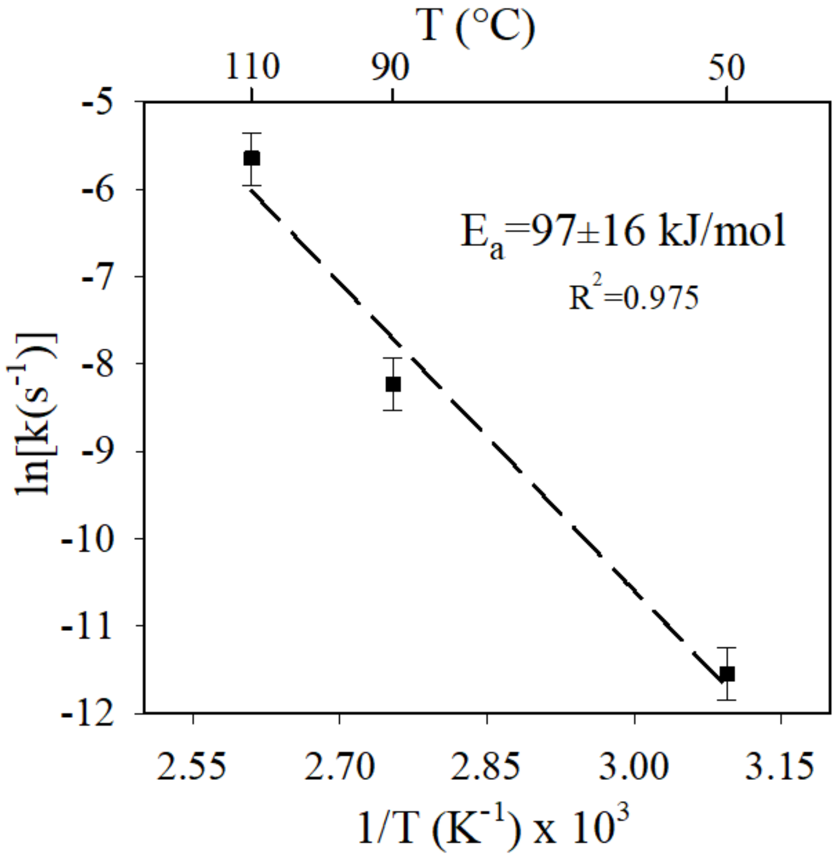
Clarifying Pyroxene Carbonation Pathways and Rates at Supercritical CO_2 Conditions Critical for Enhancing and Predicting Mineralization

Hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] precipitates on amorphous $MgSiO_3$ highlights the controlling influence of silicate substrate

Real-time in situ monitoring of mineral phase abundances with high pressure XRD at 90 bar $scCO_2$ and 50-110 °C



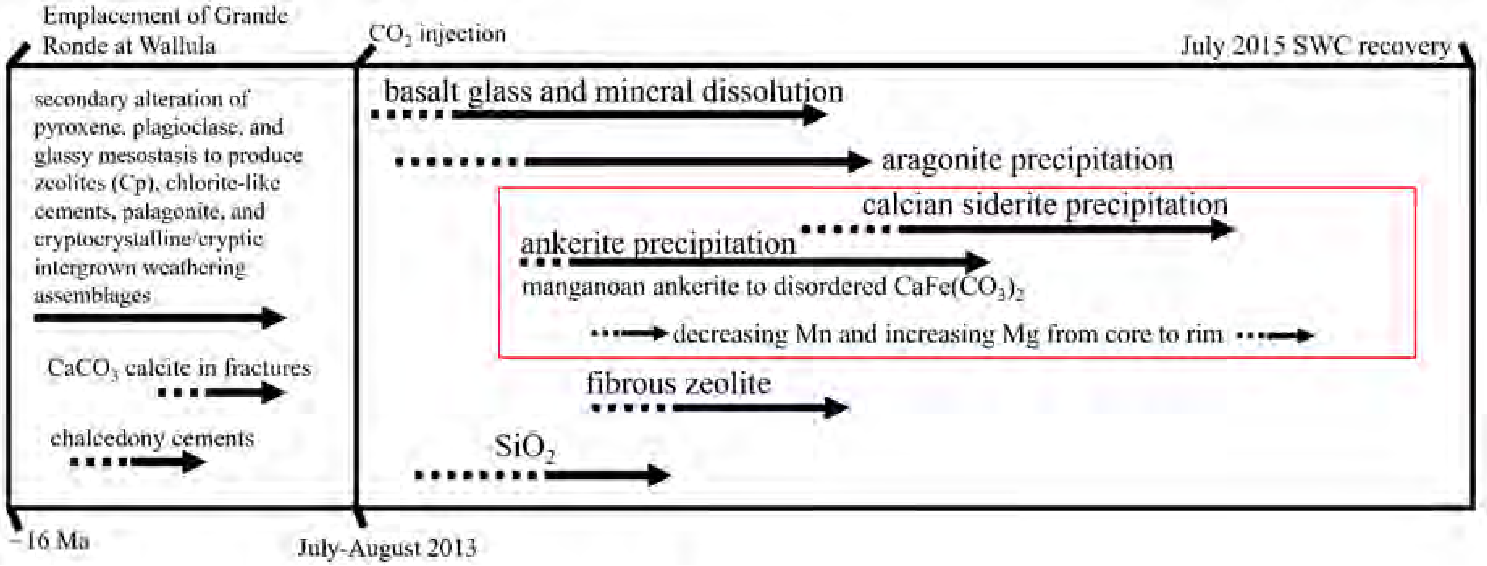
Temperature dependence of reaction rates used to parameterize reactive transport simulators



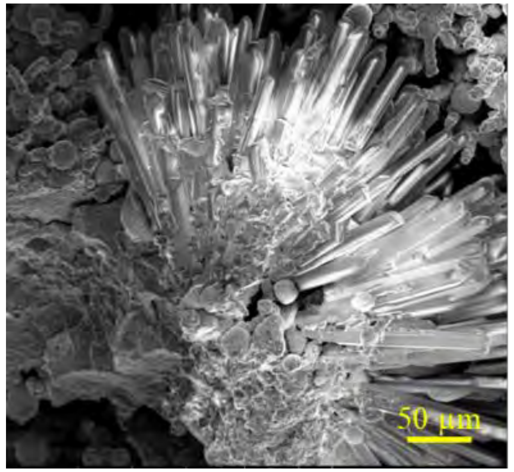
Hardee et al., Distinct Carbonation Reaction Pathways for Enstatite and Amorphous $MgSiO_3$ at Conditions Relevant to Carbon Storage in Mafic-Ultramafic Rocks. In prep for ES&T.

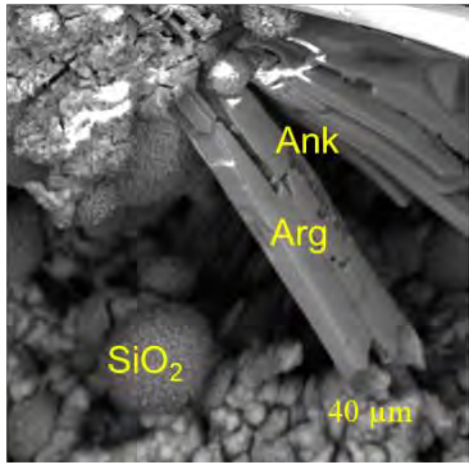
Aguila et al., Kinetics and pathways of complex Ca- and Mg- carbonate precipitation: Diopside huntinization insights for carbon mineralization in mafic-ultramafic rocks. In prep for Environmental Science: Nano

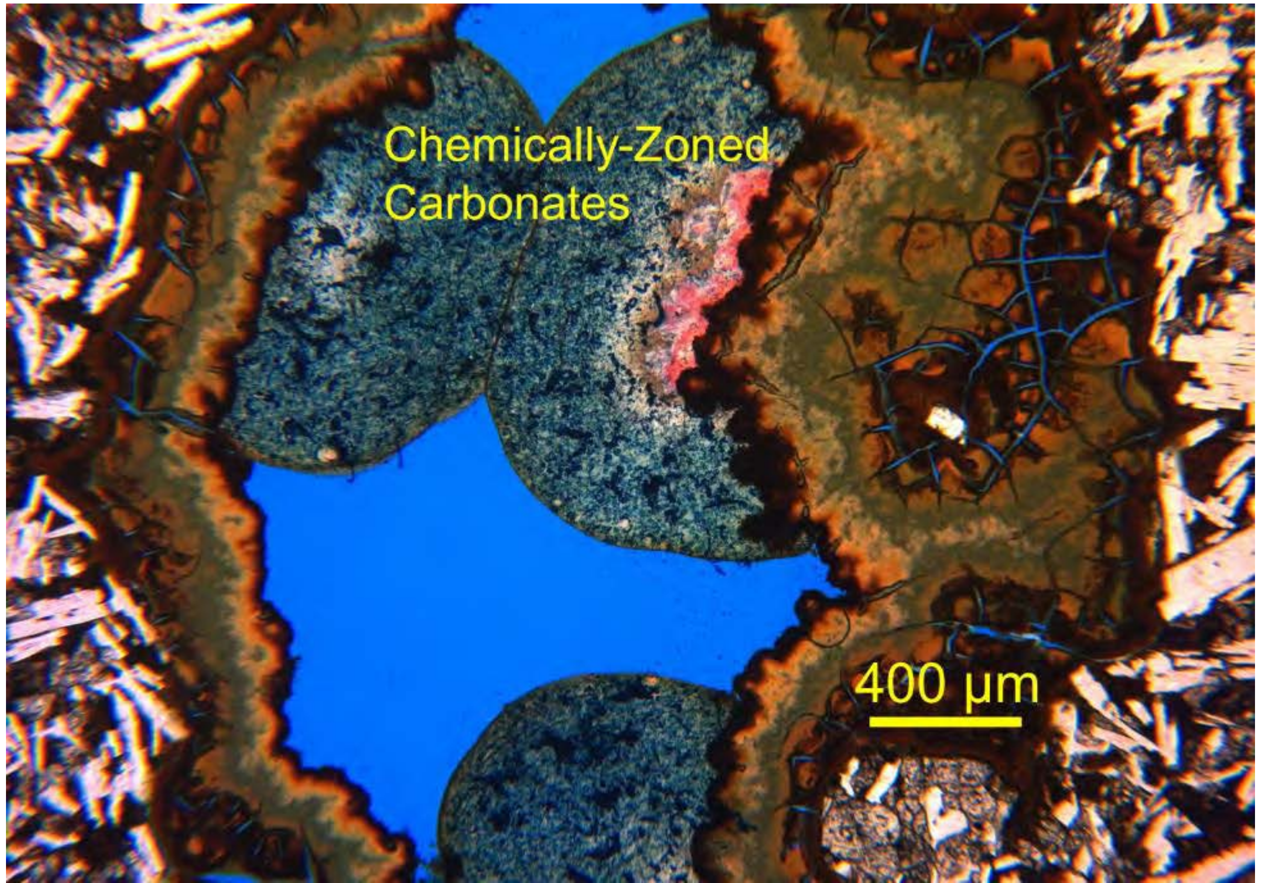
Exotic Carbon Mineralization Paragenetic Sequence Revealed



- Aragonite, amorphous silica, and fibrous zeolite-like phase result from CO_2 injection (fate of Al and Si resolved)
- Mn-rich ankerite to Ca-rich siderite composition from core to rim
- Endmember ankerite [$CaFe(CO_3)_2$] composition at core-rim transition
- Information is being used to parametrize reservoir models and elucidate fate of mobilized basalt components



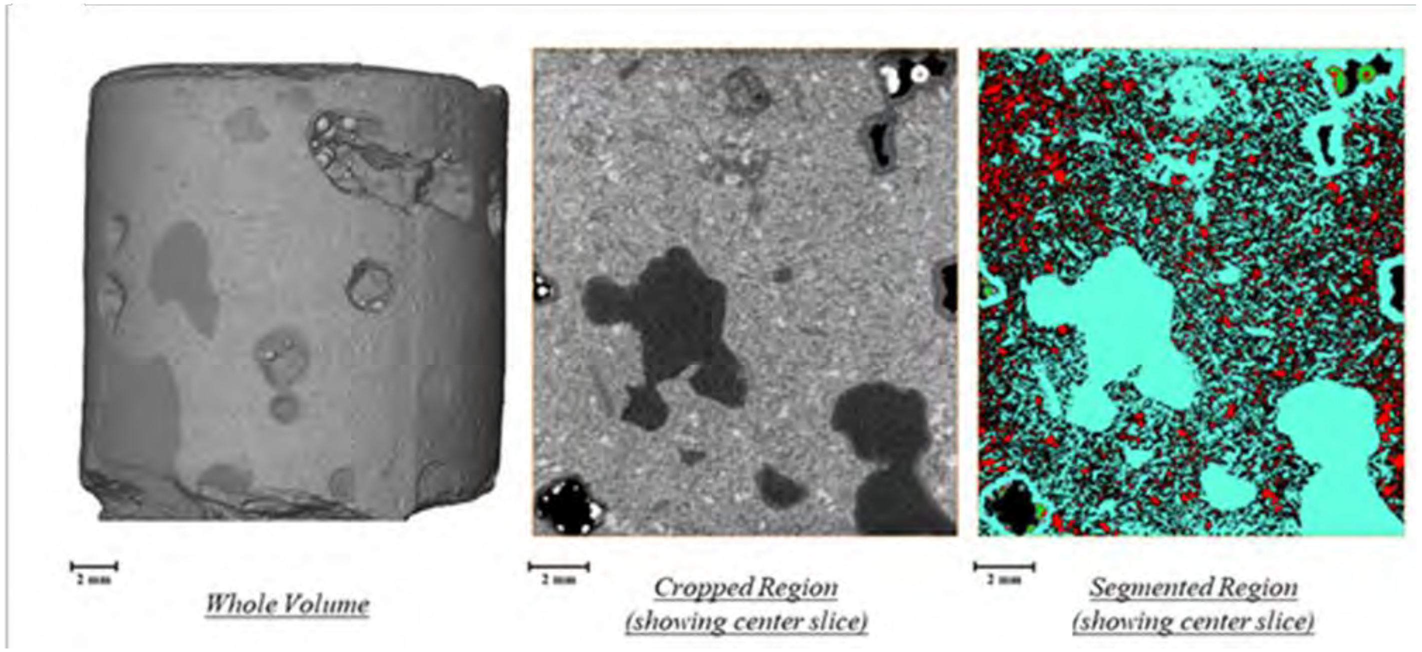




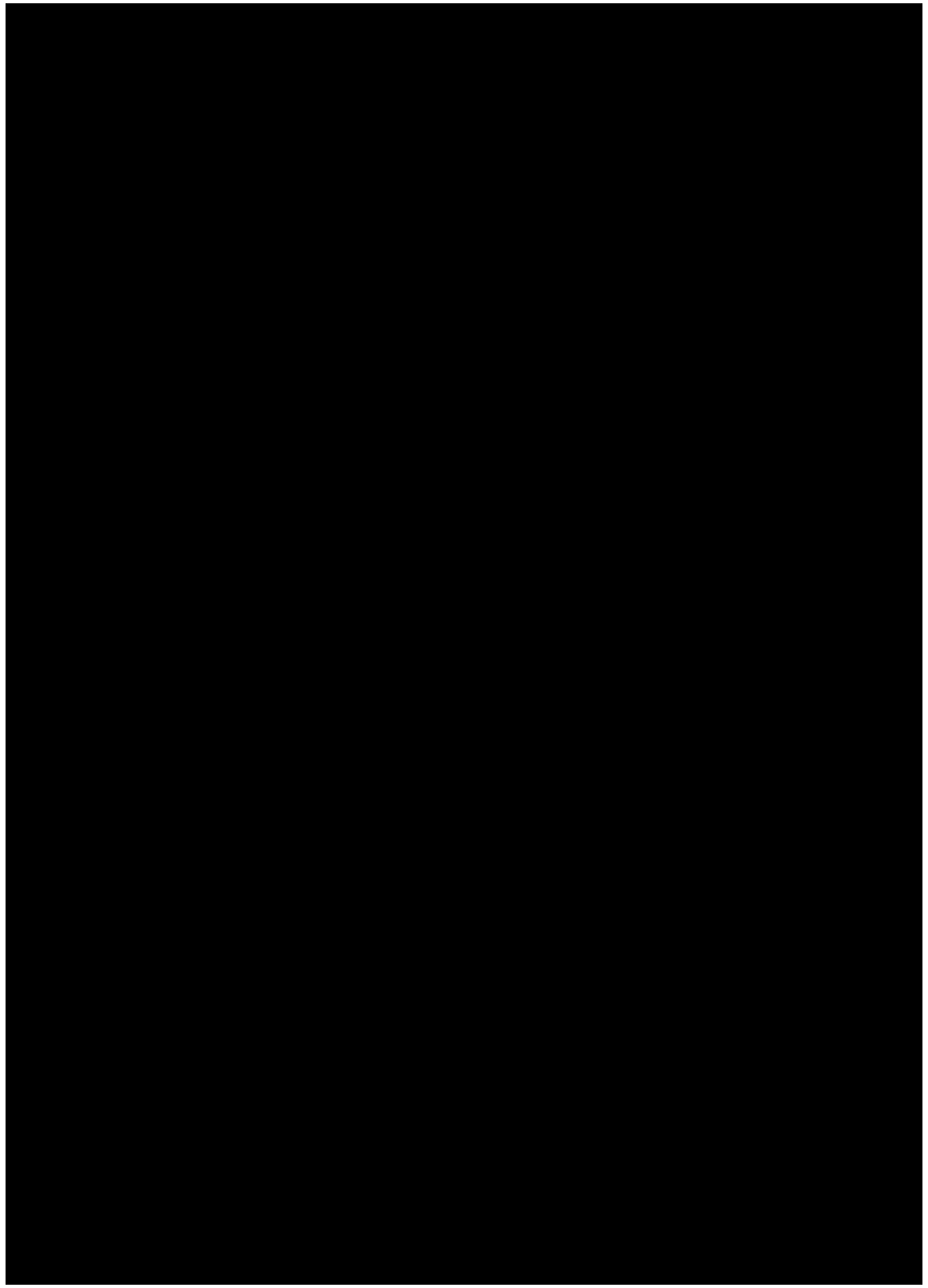
- Polites et al. 2022, *Exotic Carbonate Mineralization Recovered from a Deep Basalt Carbon Storage Demonstration*, In Review at ES&T
- Horner et al. 2022, *Intertek Basalt Core Analysis Report*, PNNL Report 30940
- Holliman et al. 2022, *Carbon Sequestration in Basalts: Sidewall Core Characterization Data from Wallula Basalt Pilot Project*, PNNL Report 32848

Quantification of Basalt Pore Network Architecture and Carbon Mineralization

- 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



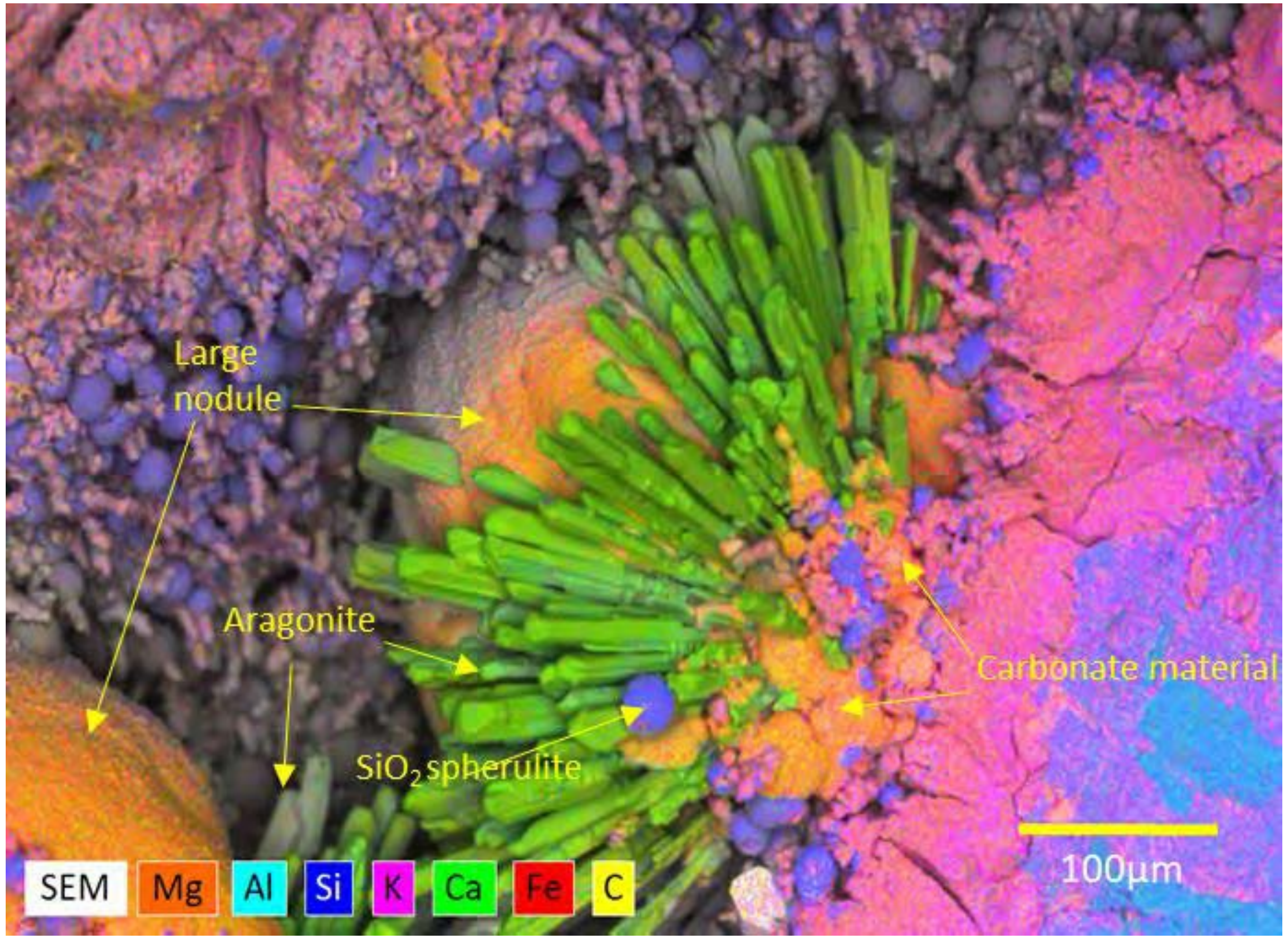
Battu et al. 2022. *Quantification of CO_2 Mineralization in Sidewall Cores Collected from Wallula Basalt Pilot Project*, in prep for ES&T



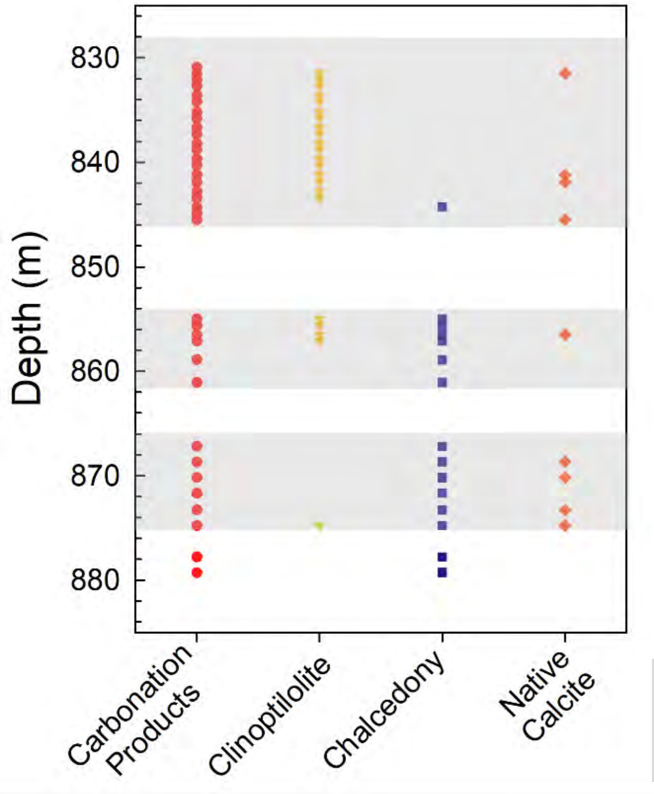
Carbonate nodules (red) imaged within a post-injection Wallula sidewall core

Pore-scale Heterogeneities in the Stacked Reservoirs Produce a Diversity of Carbonation Pathways

- Most in-depth petrographic study of the Wallula samples to date
- Further insight into relationship between aragonite and ankerite/siderite nodules
- Morphology of nodule core varies from spherical-rhombohedral-acicular



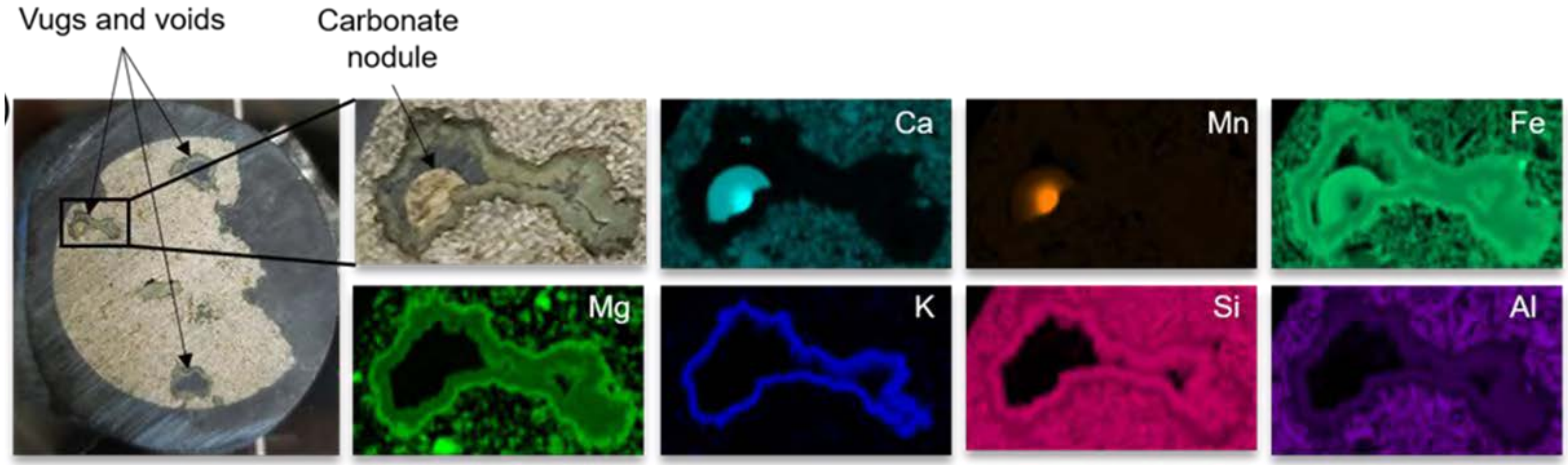
- Diversity of carbonate size, morphology, and chemistry correlates with pore-lining phase
- Cryptic variability in enigmatic chlorophaeite precipitates

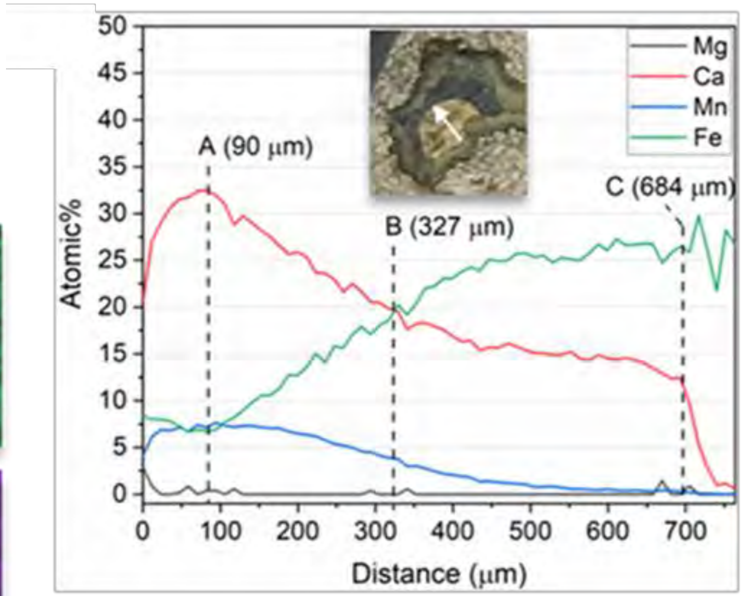


Depp et al., *Pore-scale Microenvironments Control Anthropogenic Carbon Mineralization Outcomes in Basalt*, In Review at ACS Earth & Space Chemistry

Spatially-Resolved Chemical Abundances and Coordination States Trace Fate and Transport of Mobilized Metals

- XRF and XPS confirm carbonate nodules may have chemical zonation with Ca-dominant, Mn-bearing cores
- Outer sections of nodules are Fe-dominant
- Comparing pre/post injection samples reveals Mn concentrated in natural pore-lining chlorophaeite
- Future work will integrate XRF, XPS, and XMT to determine how microenvironments control mobilization and scavenging of metals, vital for interpreting water chemistry evolution and constraining reactive transport models

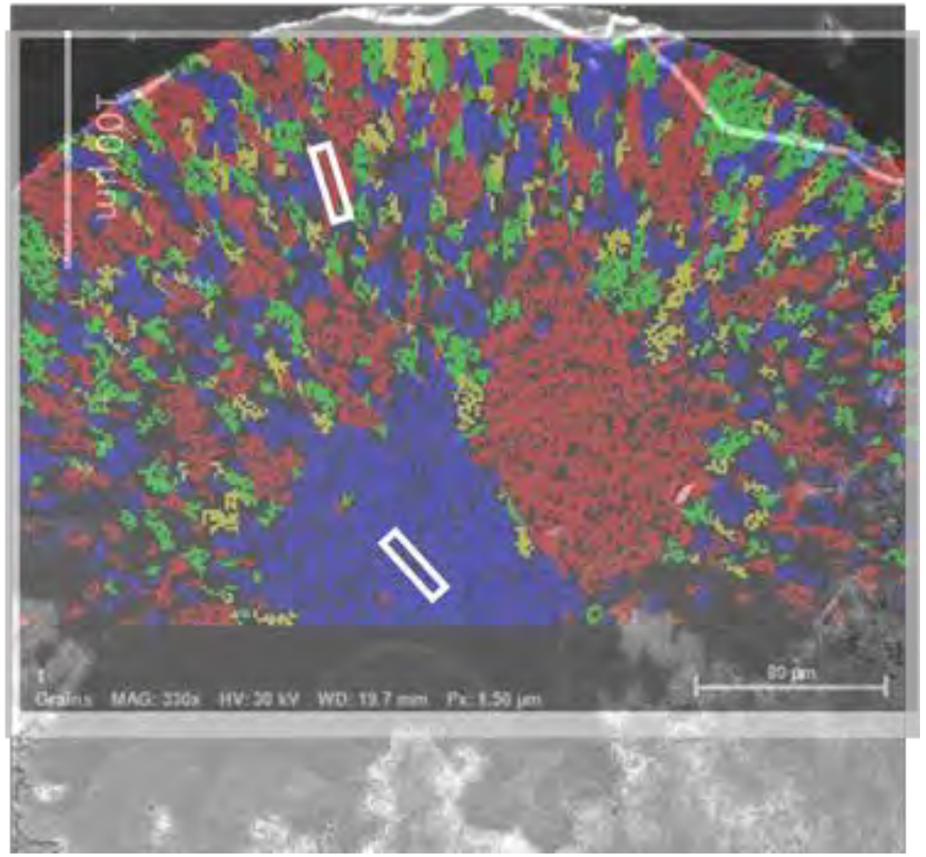




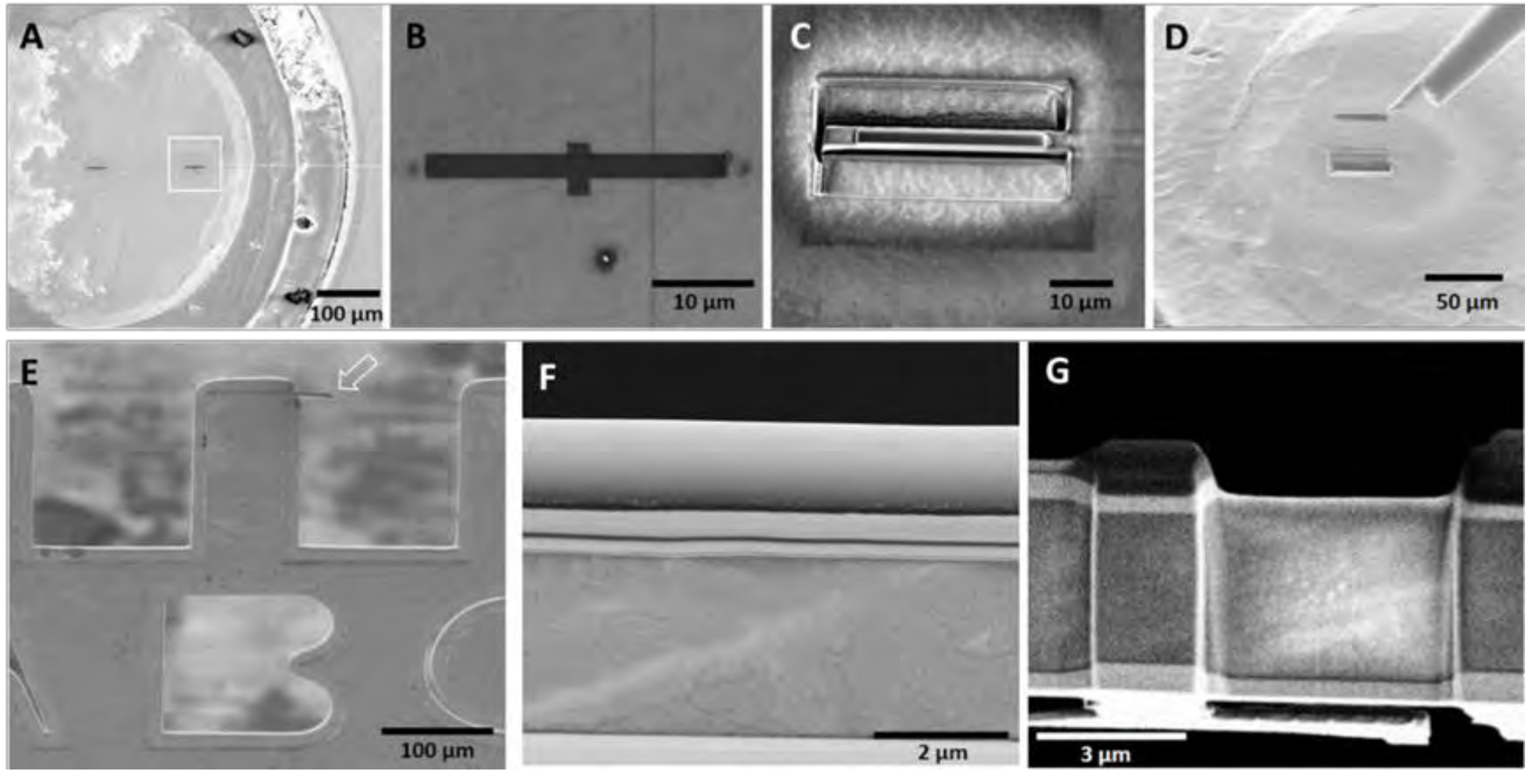
Lahiri et al. 2022, *TBA*

Nanoscale Insights Into Mn-Fe-Ca Carbonate Growth Mechanisms and Outcomes

- Mn- and Fe-bearing sections of carbonate nodule extracted
- Critical mass of capabilities: EBSD, SEM, STEM, EDS, SAED, FIB, APT
- Nanoscale resolution for examining carbonate precipitates
- Initial results elucidate roles of oversaturation and structure-chemistry relationships



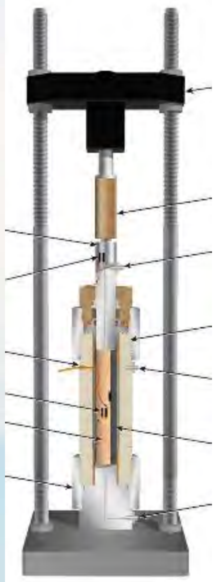
EBSD reveals spherulitic texture of Fe-rich region, consistent with optical microscopy



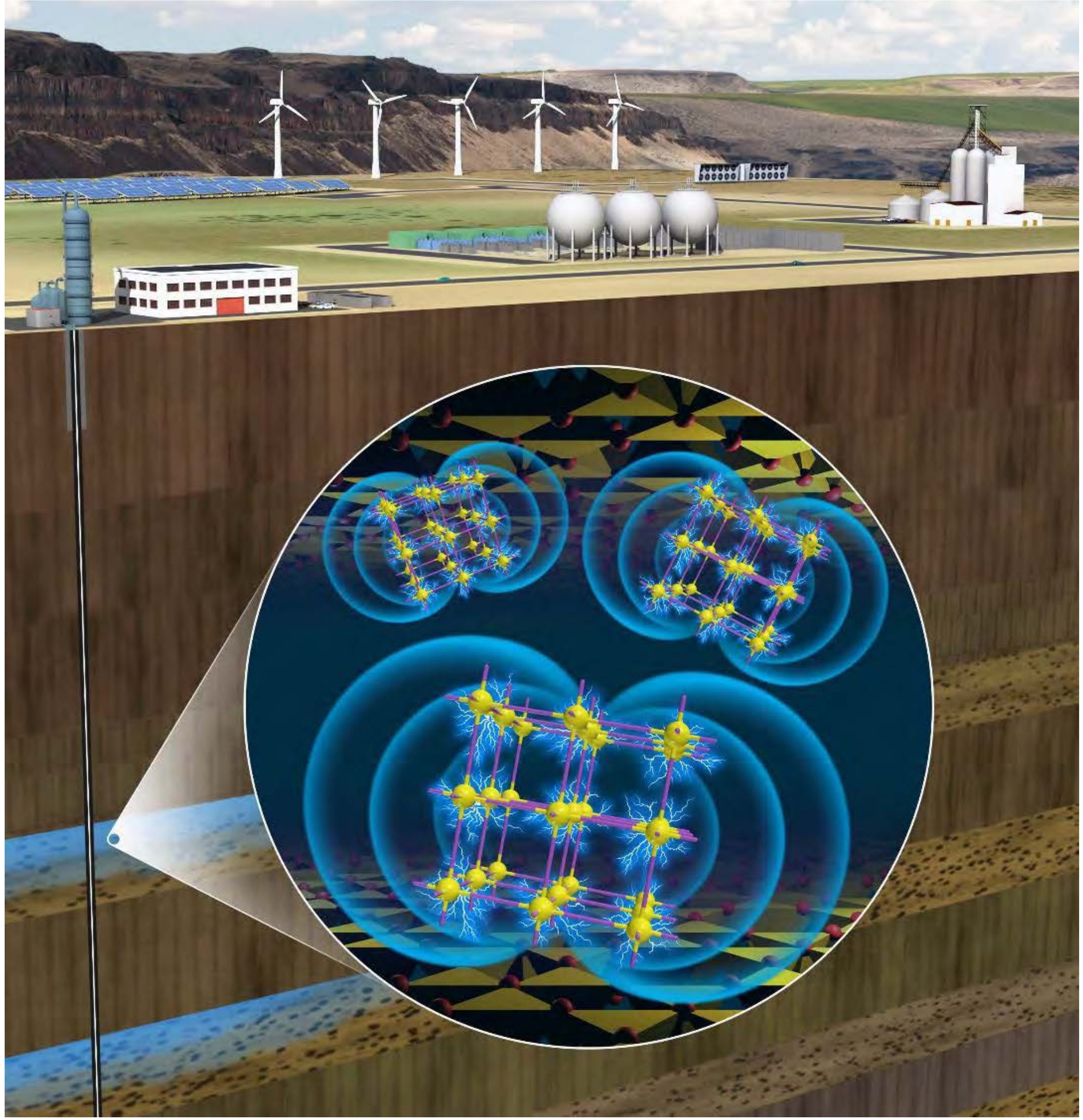
SEM images highlighting the steps involved in TEM lamella preparation using focused ion-beam milling techniques.

Taylor et al. 2022. *TBA*

Transformational Approaches to Geophysical Monitoring with Metamaterial Contrast Agents



- Current monitoring techniques for detecting and surveying injected CO_2, other fluid mixtures, and fracture networks suffer from low detection sensitivity and limited volumetric resolution
- Injectable colloidal nanoparticles influence elastic/anelastic properties of rocks (Young's modulus and attenuation)
- Forward seismic modelling illustrates unprecedented enhancement of
- Multimodal sensing responsive to near-wellbore NMR and Electrical surveys also



- Miller et al. 2022, ACS Applied Materials and Interfaces, https://doi.org/10.1021/acsami.2c03187
- Miller et al. 2018, ACS Applied Materials and Interfaces, https://doi.org/10.1021/acsami.8b19249
- Miller et al. 2019, URTeC, https://doi.org/10.15530/urtec-2019-1123
- Schaef et al. 2017, Energy Procedia, https://doi.org/10.1016/j.egypro.2017.03.1506
- Holliman et al., submitted to Materials Advances
- Nune et al., in review at Scientific Reports

Integrated Workflow will Enable De-risking of Rapid and Permanent Carbon Storage in Basalts

Task 1 Regional Geologic Model

Task 2 Numerical Simulation

Task 3 Preliminary Site Screening

Task 4 Characterization, Permitting, and Development Planning

Task 5 Stakeholder Engagement

Deliverables

1. Journal manuscript detailing regional geologic model and preliminary capacity estimates;
2. Deliverable: Journal manuscript detailing regional CO_2 storage reactive transport simulation results, including uncertainty quantification and sensitivity analysis on key parameters.
3. Report describing prioritized list of potential sites for additional pre-drilling data acquisition and/or characterization well(s).
4. Final report detailing permitting and development feasibility, including cost estimates and recommendations.
5. Regional stakeholder workshop report.

Acknowledgments

This work was sponsored by
Carbon Utilization and Storage Partnership (CUSP)
Office of Fossil Energy Carbon Management
Darin Damiani
National Energy Technology Laboratory
Department of Energy
SC WDTS