Resource Assessment of Geological Formations and Mine Waste for Carbon Dioxide Mineralization in the US Mid-Atlantic

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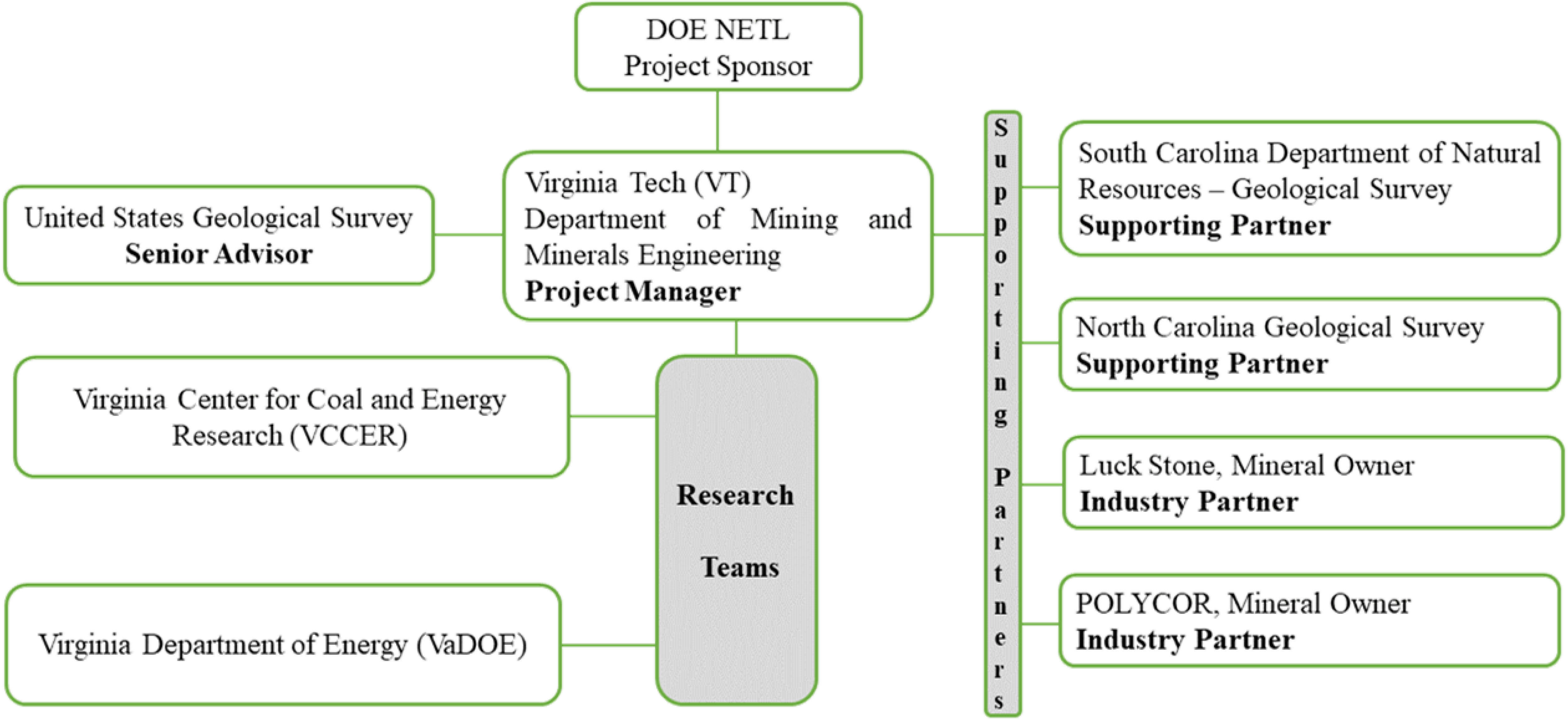
Outline

- Our team
- Project objectives
- Background information
- Methodology, tasks, and milestones
- Community benefits plan
- DEIA plan
- Project benefits

Our team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Industry Partner
POLYCOR, Mineral Owner
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Research team

- **Bahareh Nojabaei (PI)**

Mining and Minerals Engineering, multiphase multicomponent flow simulation, molecular simulation, machine learning and data analysis

- **Rohit Pandey (Co-PI)**

Virginia Tech Mining and Minerals Engineering, rock mechanics

- **Ryan Pollyea (Co-PI)**

Virginia Tech Geosciences and VCCER, reactive transport modeling

- **Nino Ripepi (Co-PI)**

Virginia Tech Mining and Minerals Engineering and VCCER, mining engineering, mine safety

- **Wencai Zhang (Co-PI)**

Virginia Tech Mining and Minerals Engineering, mineral processing

- **Jenny Meng**

Virginia Department of Energy, geology

Primary objectives

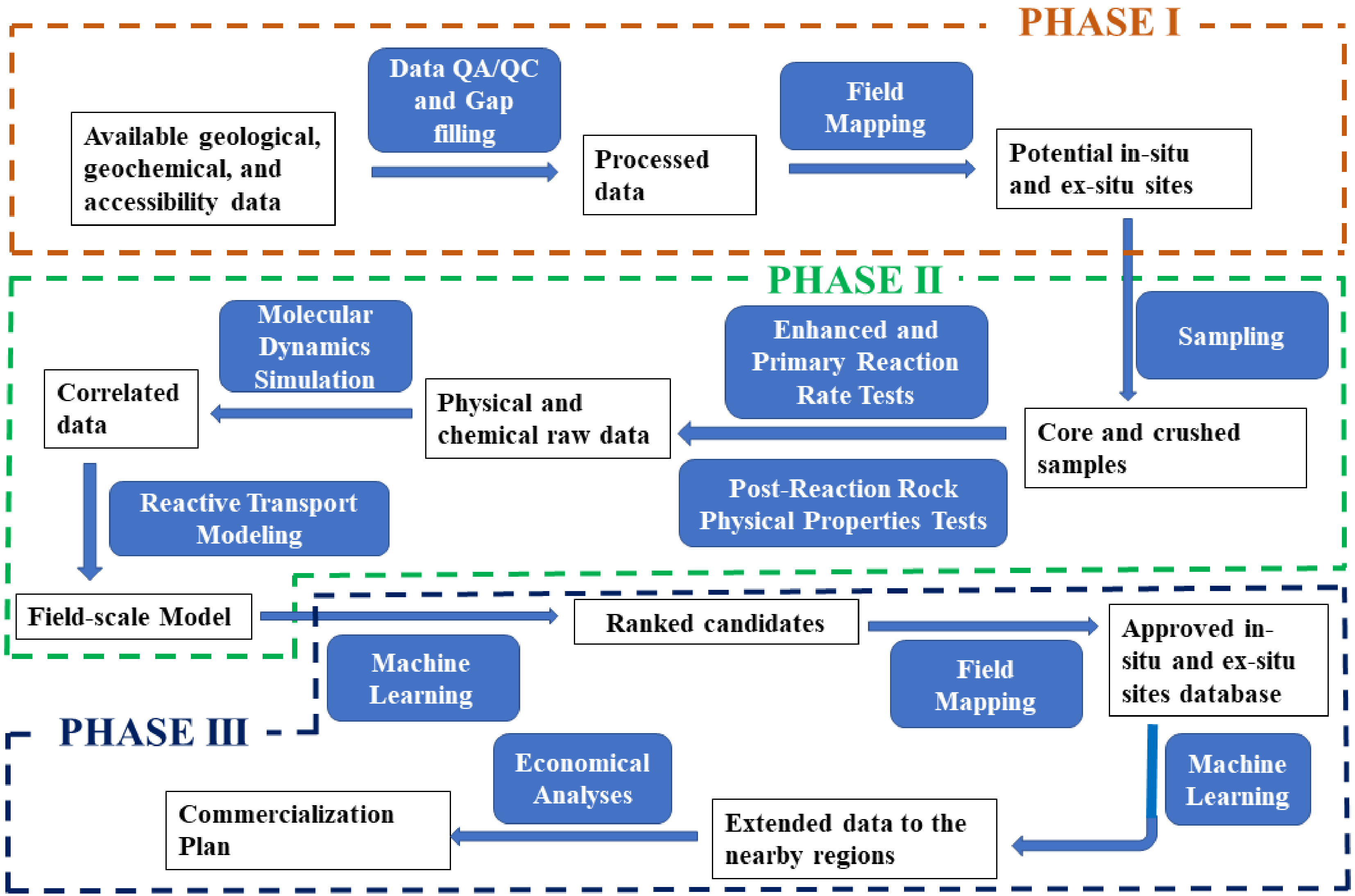
- Analyze the geological data in the US Mid-Atlantic region, and search for potentially suitable rock types.
- Assess the suitability of target formations and rocks for efficient and timely reactions through performing laboratory scale CO_2 mineralization reaction tests.
- Assess the post-mineralization properties of rocks through laboratory scale tests and molecular scale simulations.
- Upscale the laboratory scale assessments to the field scale, through reactive transport modeling and simulation, and regression analysis.
- Rank the candidates in terms of their suitability for carbon storage, through using machine learning and inclusion of multiple factors such as reaction rates, rock properties, accessibility, and mineralization associated costs.
- Extend and extrapolate our understanding to nearby regions, through using machine learning.
- Provide a database and map the carbon storage resources.

Multiscale data-driven framework

Phase I: Geological pre-study assessment, mapping, and data filtering

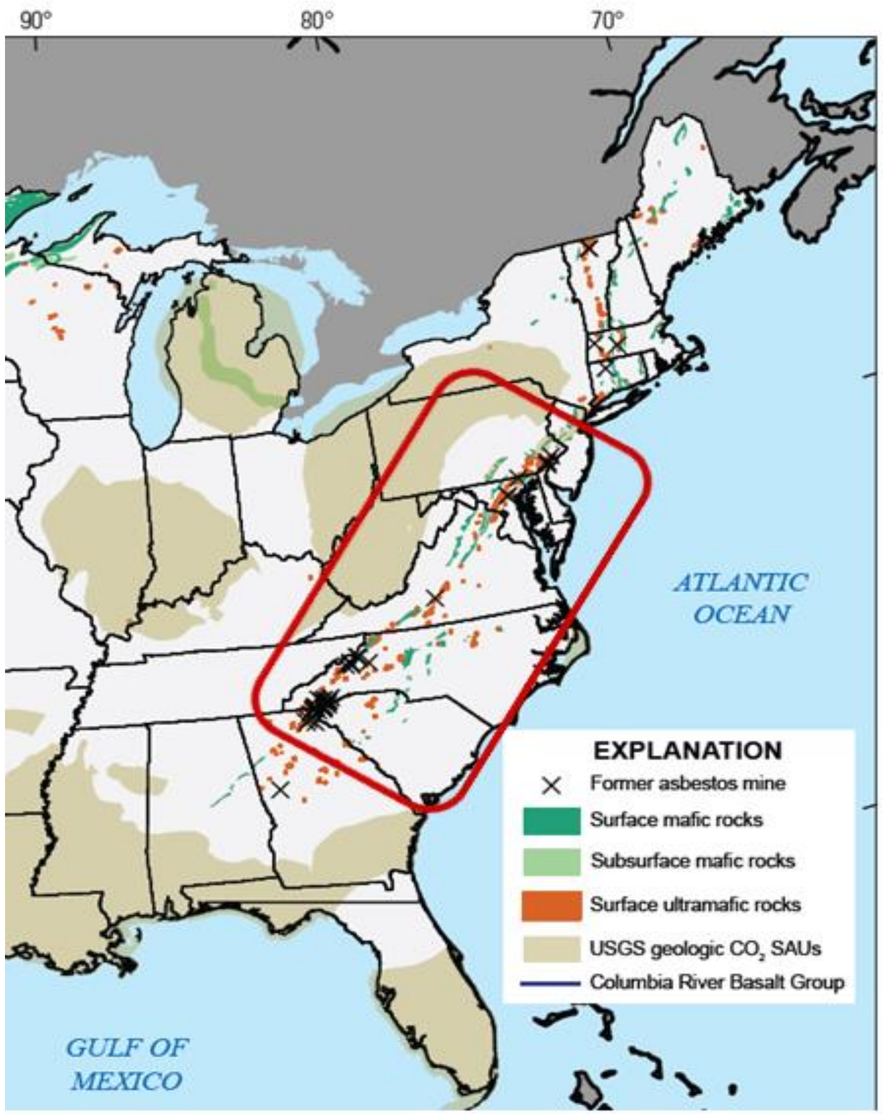
Phase II: Multiscale CO_2 mineralization characterization

Phase III: Post-study mapping, database development, and commercialization



Carbon mineralization potential

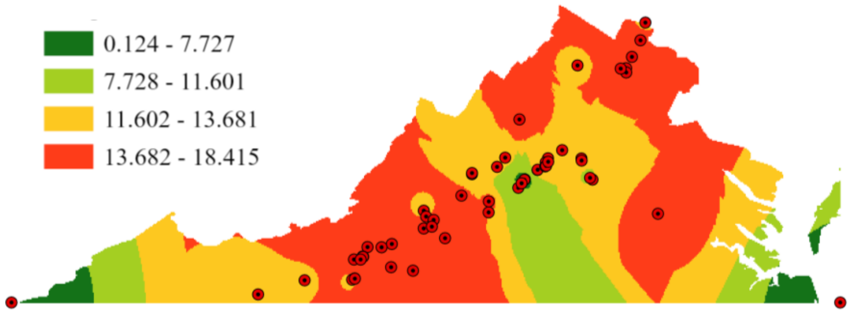
- The CAMP deposits within the US Mid-Atlantic States contain both **mafic and ultramafic** rocks with high concentrations of desired cations (e.g. Mg^{2+}, Fe^{2+}, or Ca^{2+}) for carbon mineralization.
- Greenstone is metamorphosed basalt and a major rock for construction aggregate of the Blue Ridge Province from central Pennsylvania in a southwesterly direction through the central part of Virginia. Mining waste resources are available in the area as greenstone is an industrial construction aggregate in Mid-Atlantic States.
- The Mid-Atlantic States also have resources of ultramafic rocks in sparse outcrops in Virginia and Maryland, as well as peridotite and serpentinites.
- A thorough resource assessment of natural materials, as well as industrial and mine wastes to be used in both in-situ and ex-situ CO_2 mineralization processes in the US Mid-Atlantic region.



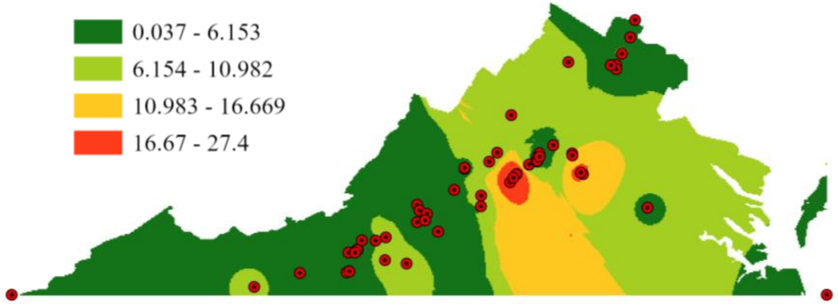
Geologic Pre-assessment and Sampling

- Assessments of mafic and ultramafic rock exposure through existing geologic database
- Gathering information on the bedrock spatial extents, depth, key formations, petrology, accessibility, and existing physical and chemical properties.
- Selection of mining sites that associate with mafic and ultramafic rock production for conducting the industrial waste investigation.
- Sample collections for lab testing effort from Virginia and other nearby states.

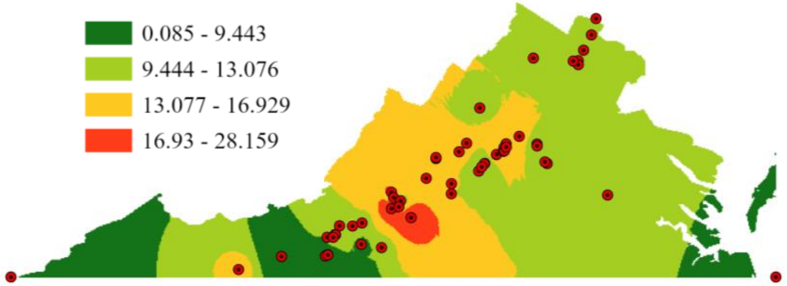
Al_2O_3



MgO



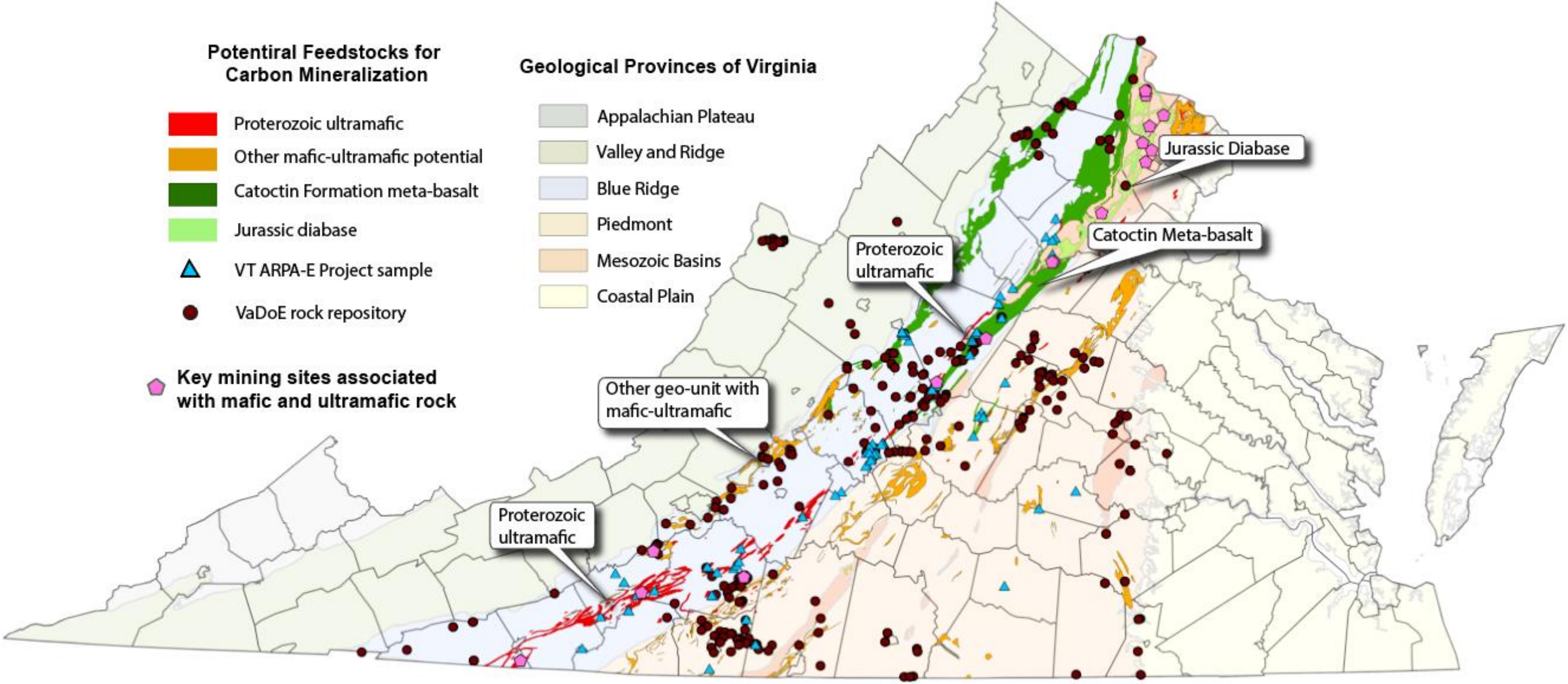
Fe_2O_3



Mining Sites and industrial waste in Virginia

Company Name	Mine Name	County	Commodity Type	Resource	Formation
Cardinal Realty (Virginia) DBA	Galax Quarry	Grayson	Amphibolite/ultramafic	Ultramafic	Ashe/Alligator Back
Polycor Virginia Inc.	#1	Nelson	Soapstone	Ultramafic	Lynchburg
Salem Stone Corporation	Floyd Quarry	Floyd	Amphibolite	Mafic	Ashe/Alligator Back
Rockydale Quarries Corp	Jacks Mountain	Franklin	Gabbro	Mafic	Ashe/Alligator Back
Luck Stone Corporation	Charlottesville	Albemarle	Basalt	Mafic	Catoctin
Granite Managers, Inc.	Granite Managers, In	Culpeper	Granite,Dimension Stone	Mafic	Jurassic diabase
New England Stone Industries, Inc	Jet Mist	Culpeper	Granite,Dimension Stone	Mafic	Jurassic diabase
Luck Stone Corporation	Bealeton Plant	Fauquier	Traprock	Mafic	Jurassic diabase
Vulcan Construction Materials, LLC	Manassas Quarry	Prince William	Traprock	Mafic	Jurassic diabase
Luck Stone Corporation	Fairfax Plant	Fairfax	Traprock	Mafic	Jurassic diabase
Luck Stone Corporation	Bull Run Plant	Loudoun	Traprock	Mafic	Jurassic diabase
Chantilly Crushed Stone, Inc.	Chantilly Crushed St	Loudoun	Traprock	Mafic	Jurassic diabase
Loudoun Quarries	Loudoun Quarries	Loudoun	Traprock	Mafic	Jurassic diabase
Luck Stone Corporation	Leesburg Plant	Loudoun	Traprock	Mafic	Jurassic diabase
Luck Stone Corporation	Goose Creek Plant	Loudoun	Traprock	Mafic	Jurassic diabase
Vulcan Construction Materials, LLC	Sanders Quarry	Fauquier	Granite/Basalt?	Mafic	Catoctin?

Potential carbon mineralization resources of Virginia

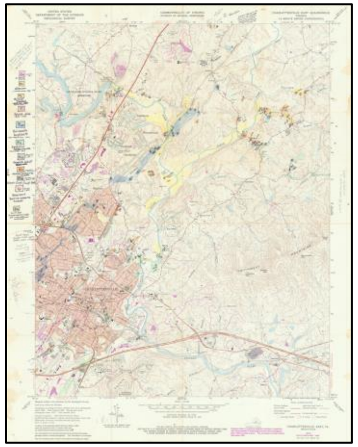


Post-field study mapping

Determined 1 candidate area for geologic mapping and 2 candidate areas for carbon mineralization (CM) feasibility study.

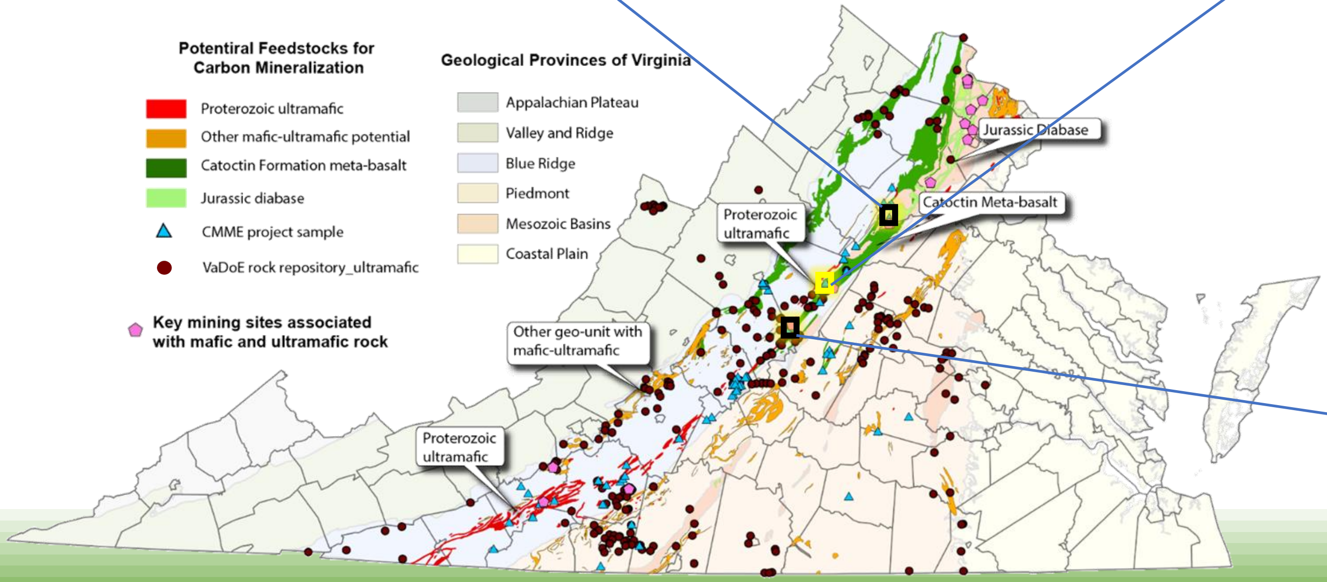
Rapidan Quadrangle

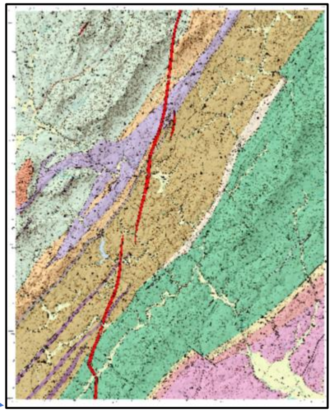
- CM Resource: diabase, metabasalt
- Available Map: 1:100K map, 1:24K unpublished field map
- Task plan: feasibility study using existing map



Charlottesville East Quadrangle

- CM Resource: Chlorite schist, amphibolite, metabasalt
- Available Map: 1:100K map, partial 1:24K draft map
- Mapping plan: geologic mapping at 1:24K scale, then feasibility study





Alberene/ Schuyler Quadrangle (Schuyler if EDMAP completed)

- CM Resource: Chlorite schist, amphibolite, metabasalt, diabase
- Available Map: 1:24K EDMAP
- Task plan: feasibility study using existing map

Laboratory analyses of reactions and product evaluation

- The goal is to evaluate **carbon mineralization efficiency**, **dissolution of various species**, and the **kinetics of the reactions** occurring in the process.
- The carbon mineralization tests will be carried out under different conditions to evaluate the effect of different parameters, such as **rock size, pressure, and temperature**.
- Mineral dissolution tests will also be performed on the samples to evaluate the extractability of critical elements, i.e **Rare Earth Elements**.
- Results from the mineral dissolution tests will be analyzed to determine **the underlying metabolic pathways in order to identify the microbial communities** potentially catalyzing host-rock dissolution.

Laboratory analyses of reactions and product evaluation

Feed particle size
Feed porosity
Feed surface area
Feed mineralogy
Reaction pressure
Reaction temperature
Reaction solids content
Reaction time
Solution chemistry
Etc.

<u>Carbon Mineralization</u>

Carbon mineralization efficiency;
Carbon mineralization kinetics;
Carbon mineralization mechanisms;
Dissolution behavior;
Product characteristics

<u>CM Recovery</u>

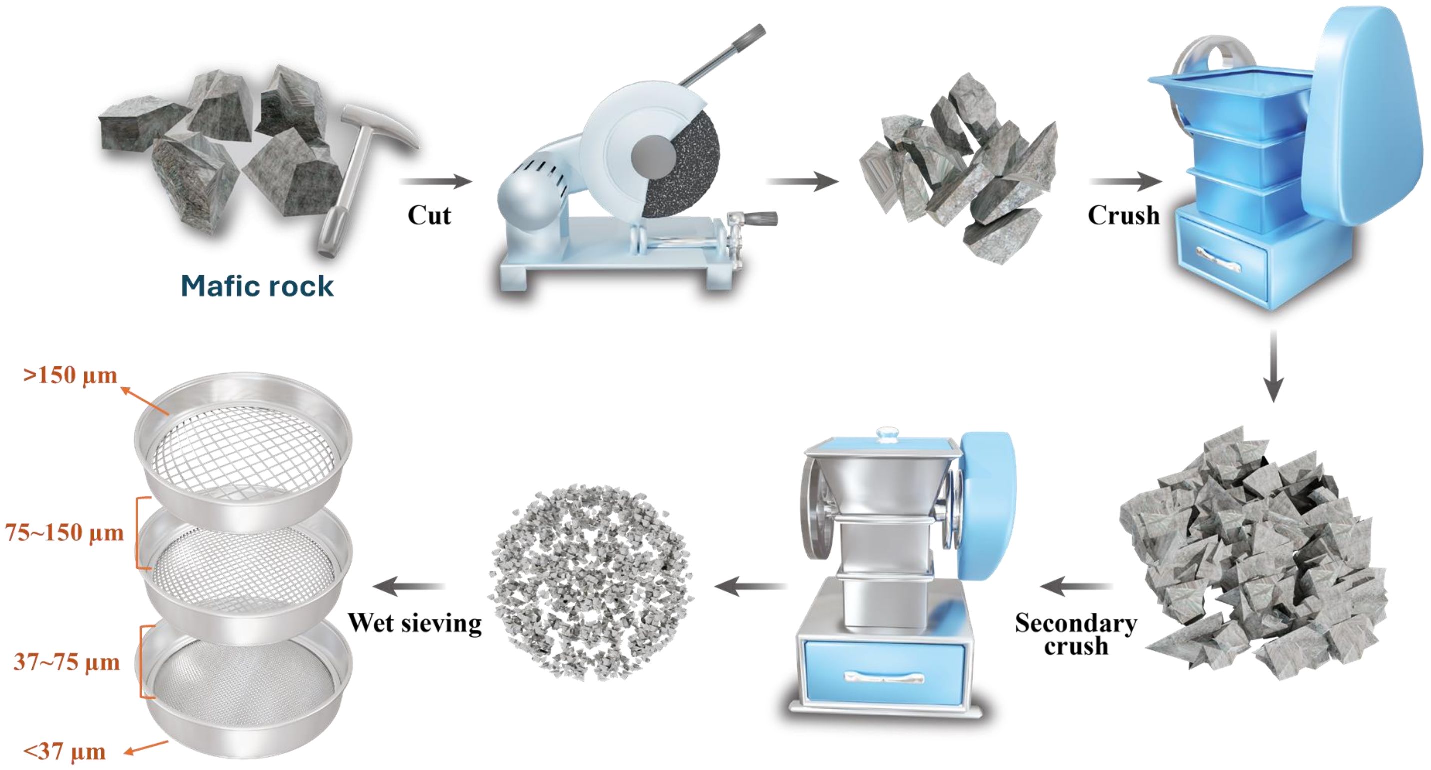
Leaching kinetics & thermodynamics of CMs and carbon-reactive species;
Metabolic pathways

CO_2

Input for other tasks

Pretreatment (crushing and screening)

Cutting, primary crushing with a jawbreaker, secondary crushing, and wet screening. The weights of the samples across various sizes are documented in Table 1.

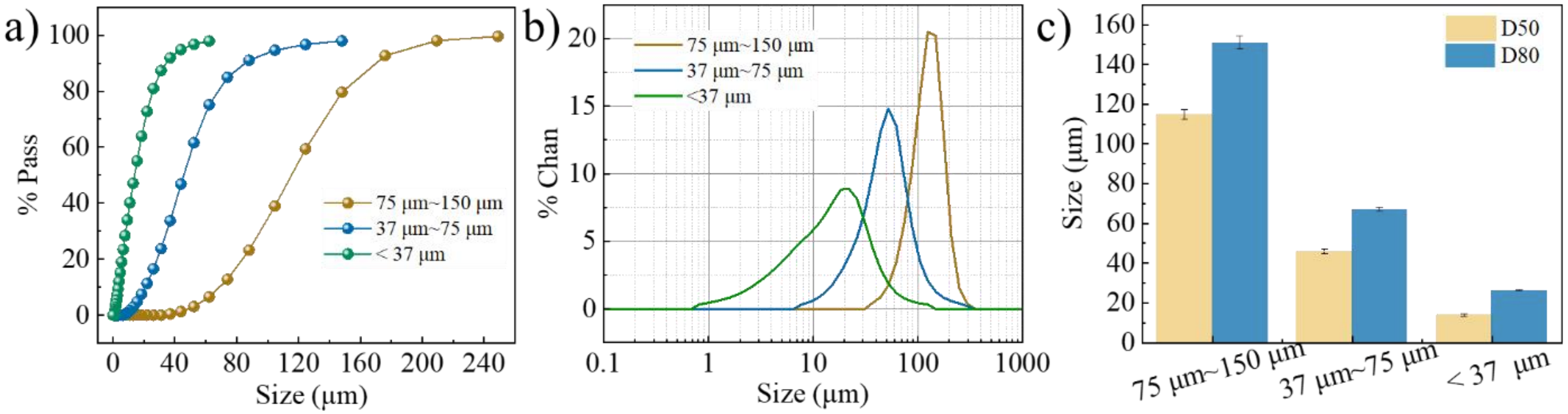


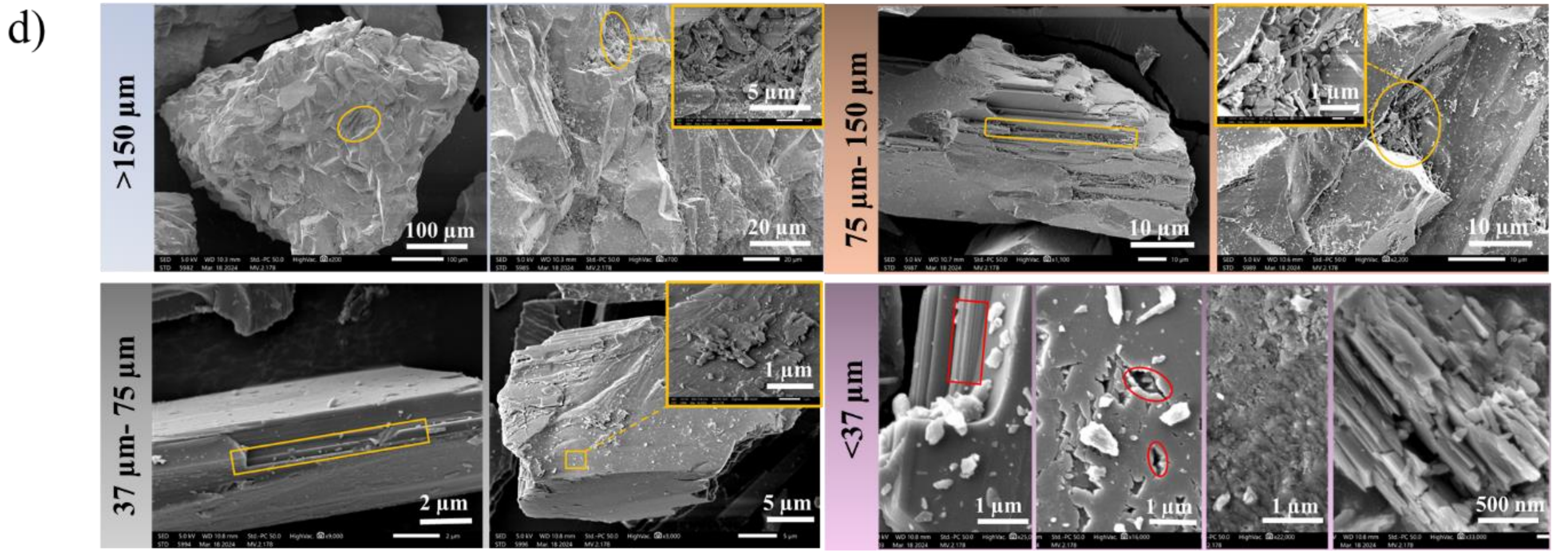
Mass percentage of different samples under different size

	Mass percentage
+150 μm	34.08 %
-150 μm~+75 μm	28.82 %
-75 μm~+37 μm	31.01 %
-37 μm	10.00 %

Physical properties and morphology

Particle size distribution of different samples





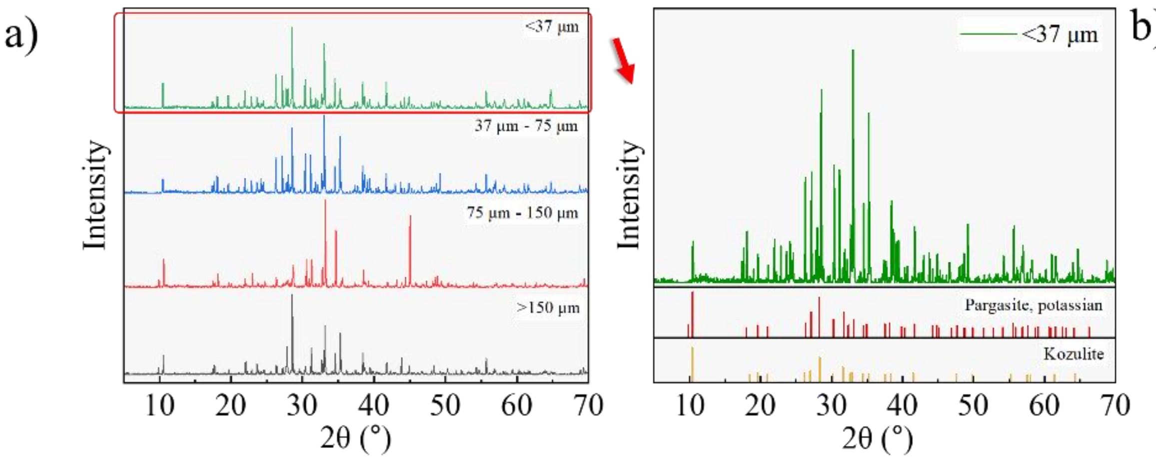
SEM images of different samples

Smaller particle size

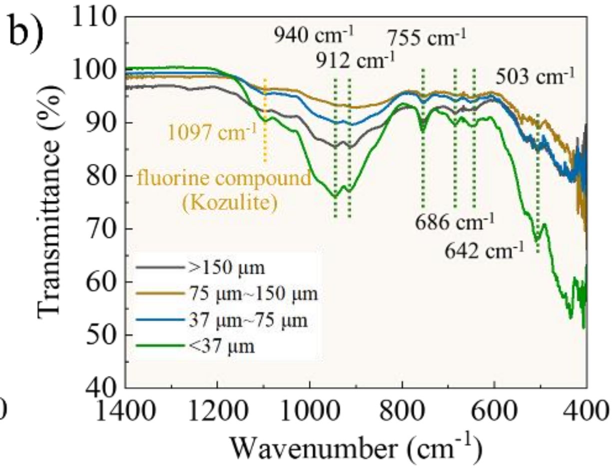
More disorganized morphology

CO_2 mineralization potential for crushed samples

XRD patterns of different samples

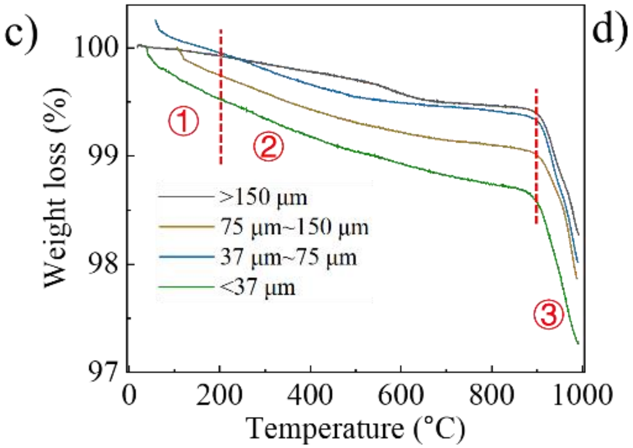


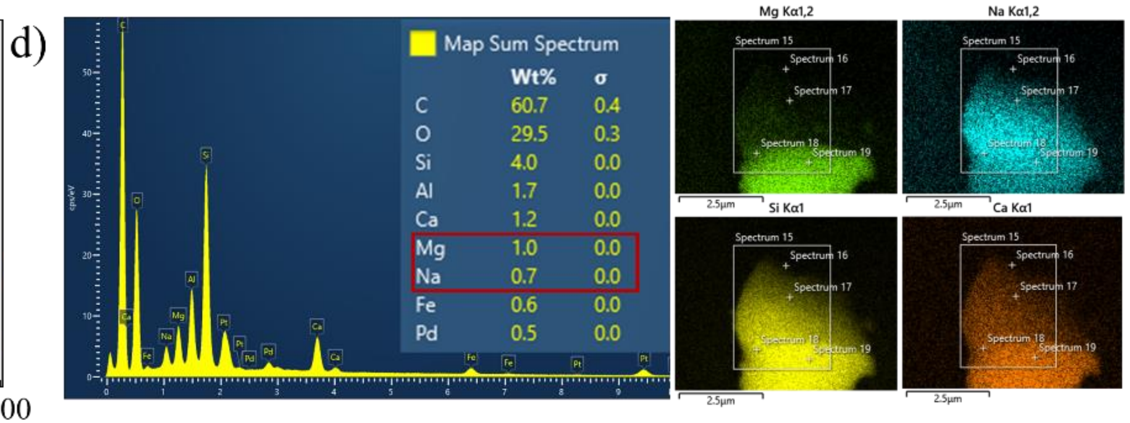
FTIR spectra



XRD: new heterogeneous peaks for the smallest particle sizes (<37 μm)

Complexity and diversity of mineral phases on the surfaces of finer particles





TGA curves

Elemental mapping of minerals below 37 μm in size

Size fraction of <37 μm demonstrated a superior potential for CO_2 mineralization.

CO_2 mineralization kinetics

To examine the CO_2 mineralization kinetics, the samples with the smallest particle size were chosen for the experiment.

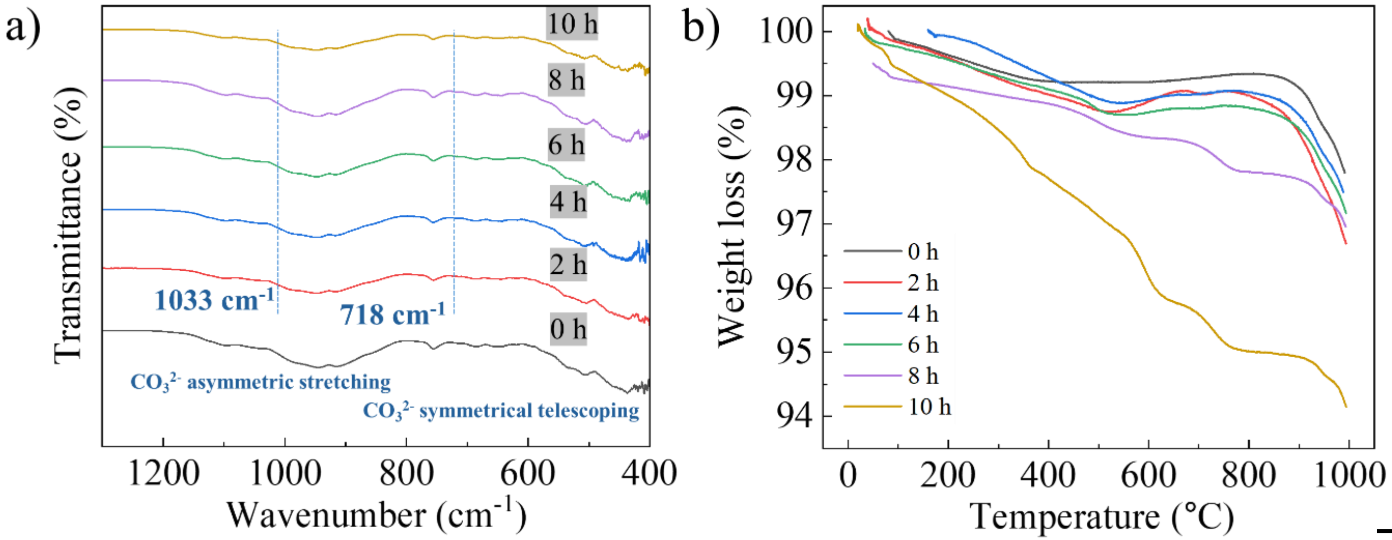
Mass of mineral (g)	Catalyzer (mL)	Temperature (℃)	Pressure (psi)	Time (h)
5 (-37 μm)	100 (1 mol/L NaCl + 1 mol/L NaHCO3)	130	750	0, 2, 4, 6, 8,10

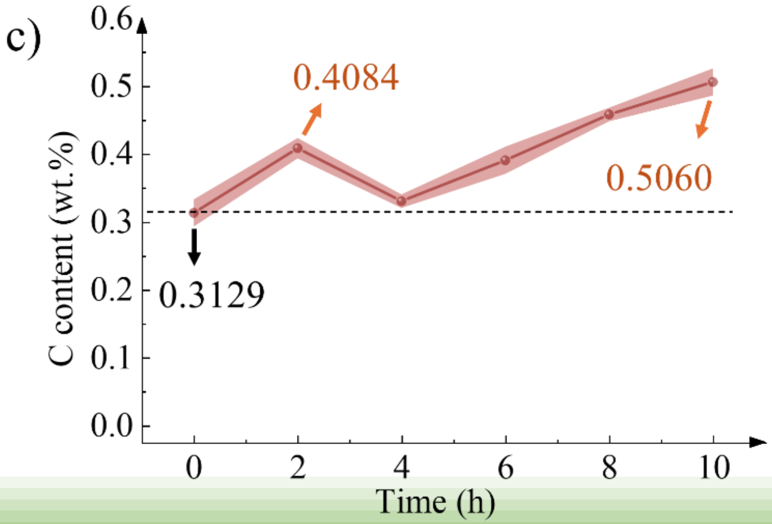
CO_2 mineralization kinetics

FTIR peaks at 1033 cm^{-1} and 718 cm^{-1}, indicative of carbonate mineral formation

The weight loss observed between 950 °C and 540 °C corresponded to the decomposition of carbonate compounds

FTIR spectra   TGA curves





$$CO_2\ sequestration\ (\%) = \frac{M_{540} - M_{950}}{M_0}$$

where M_{540} and M_{950} refer to the mess loss at 540 °C and 950 °C, respectively, while M_0 means the initial sample mass.

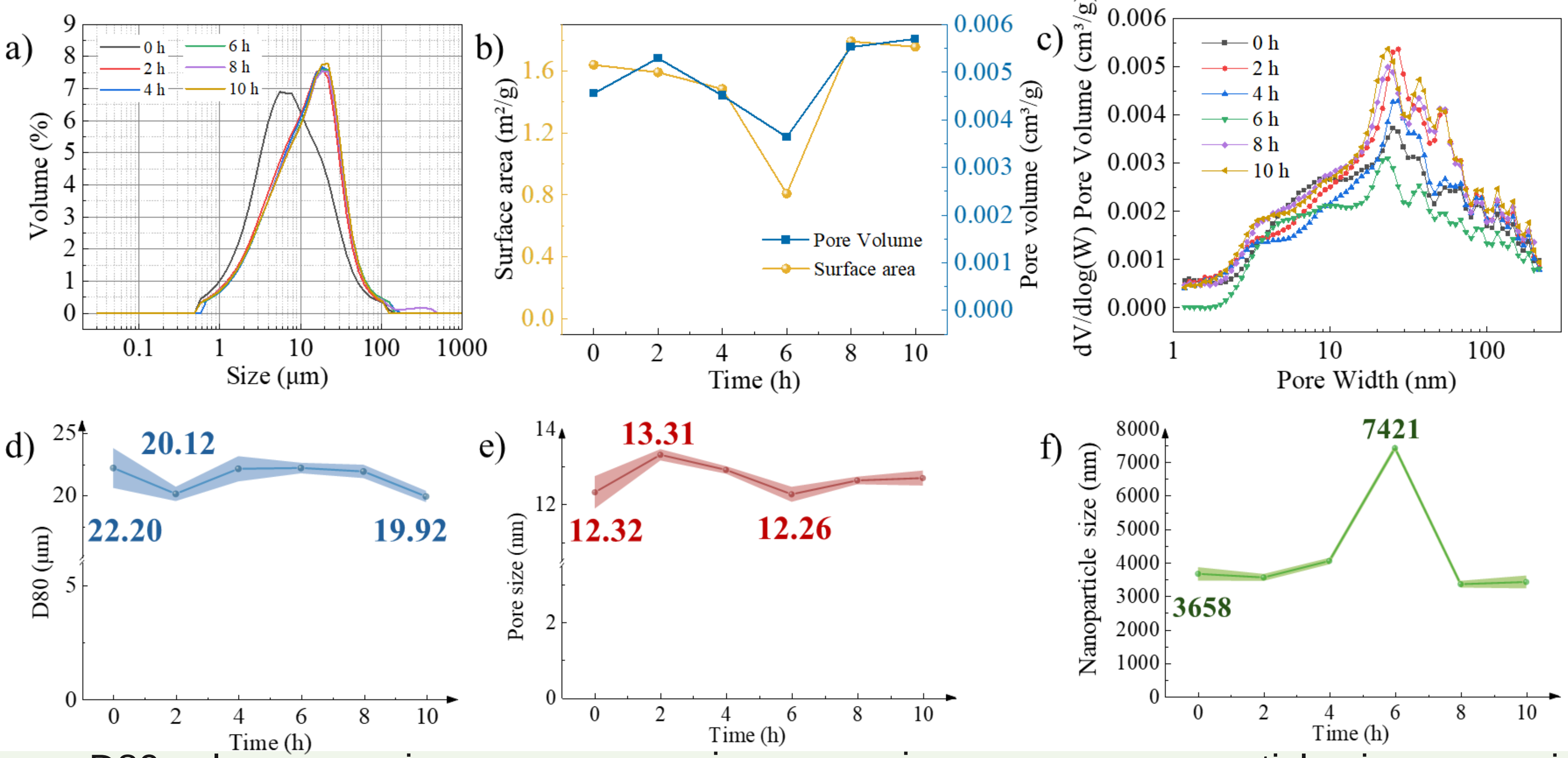
Time (h)	M_{540}	M_{950}	M_{540}-M_{950}	CO_2 sequestration (%)
0	99.21	98.48	0.73	-
2	98.76	97.58	1.18	1.62
4	98.89	98.08	0.81	1.11
6	98.71	97.88	0.83	1.14
8	98.44	97.39	1.05	1.44
10	96.87	94.65	2.22	3.04

- **No consistent single trend in CO_2 mineralization kinetics.**

Mechanism of CO_2 sequestration

- CO_2 mineralization results in the reorganization of physical structures.

Particle size distribution — Surface area and pore volume — mesoporous distribution



D80 value comparison — pore size comparison — nanoparticle size comparison

Future plan

1. **Investigate larger size (~ 1 cm) of gabbro rock**

- ❑ CO_2 mineralization kinetics (duration: 0.5 day, 1 day, 2 days, 4days, 6 days).
  - ❑ optimal temperature investigation (120 °C, 150 °C, 180 °C).
  - ❑ optimal pressure investigation (600 psi, 750 psi, 900 psi).
  - ❑ liquid-to-solid ratio: 20 mL/5 g , 50 mL/5 g , 80 mL/5 g (the catalytic solution comprised 1 mol/L NaCl and 1 mol/L $NaHCO_3$)
    - ❖ *performance:* carbon analyzer, TGA.
    - ❖ *other characterizations:* XRD, BET, FTIR, SEM mapping, etc.

2. **Investigate CO_2 mineralization potential of other samples**

  - ❑ pretreatment: grind to finest one (<37 μm) using crusher and wet screening methods.
  - ❑ CO_2 mineralization potential experiments using the finest one (<37 μm)
    - I. <u>duration:</u> 2, 4, 6, 8, 10 hours,
    - II. <u>temperature</u>: 120 °C, 150 °C, 180 °C,
    - III. <u>pressure</u>: 600 psi,750 psi, 900 psi,
    - IV. <u>liquid-to-solid ratio</u>: 20 mL/5 g , 50 mL/5 g , 80 mL/5 g (the catalytic solution comprised 1 mol/L NaCl and 1 mol/L $NaHCO_3$)
    - ❖ *performance:* carbon analyzer, TGA.
    - ❖ *other characterizations:* XRD, BET, FTIR, SEM mapping, etc.

Laboratory analyses of rock physical properties

The laboratory analysis of flow-coupled-geomechanical properties of reservoir rock will be assessed to evaluate:

a) Effect of CO_2 mineralization on the structural/textural properties of the rock type;
b) Dynamic evolution of permeability of reservoir rock with continued CO_2 mineralization.

- Determination of strength, shear/bulk modulus and failure envelope of samples pre- and post-mineralization for representative samples from the Central Atlantic Magmatic Province CAMP region.
- Using flow-through permeameter, both artificially fractured plugs and intact cores plugs will be evaluated to understand the effect of reactive surface area on mineral dissolution and carbonate precipitation rates at multiple timepoints. The change in permeability will also be measured.
- Using a scanning electron microscope and a micro-CT, providing high resolution understanding of the effect of CO_2 mineralization on the flow and structural properties of reservoir rocks.

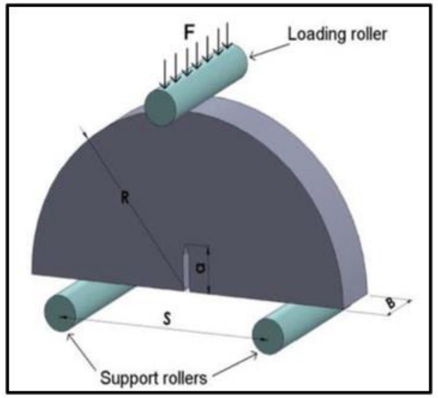
Sample size adjustment for Geomechanical Assessment

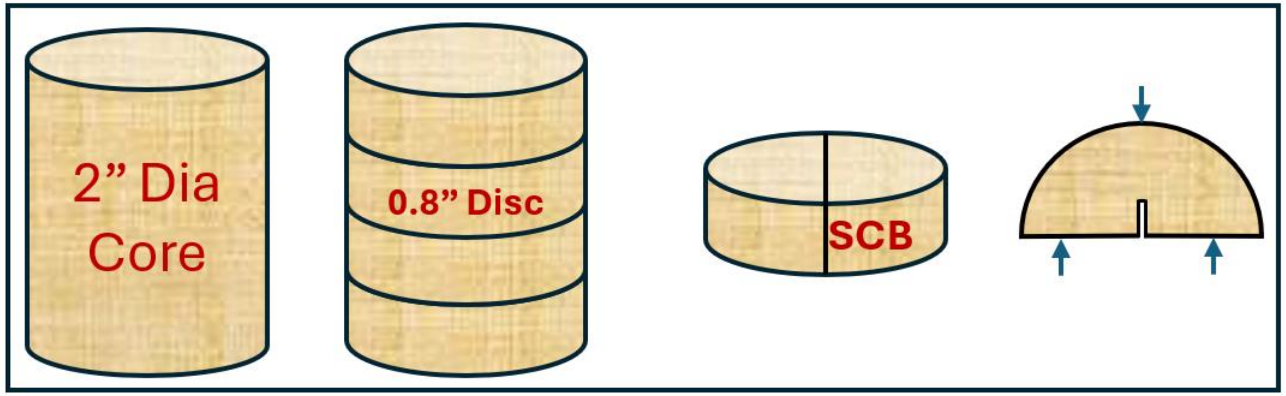
Pre-cursor to Geomechanical Assessment:

- Rate kinetics for assessing mineralization potential ongoing using crushed samples
- Crushed samples provide larger surface area for reaction – Not suitable for geomechanical analysis for in-situ applications
- Scale effect – The mineralization rate kinetics for selected target rock types will be re-established
    - Sample size ~1 cm x 1 cm x 0.5 cm
- Upon identification of appropriate rate-kinetics, larger samples typical of standard geomechanical tests will be evaluated

Fracture toughness assessment

- Objective
  - Evaluate the change in fracture toughness of selected mafic and ultramafic rocks from the CAMP region when subject to CO_2 mineralization
- Primary experimental method
  - The mode-1 fracture toughness will be evaluated using the semi-circular bend (SCB) test
  - Additional characterization tests include imaging (SEM-EDX, uCT), XRD/XRF characterization, etc.





Experimental plan

- Baseline Measure
- No. samples: 3
- Measure K_{IC}

STAGE 1

- No. samples: 18
- CO_2 Mineralization
- SEM-EDX and/or uCT (Before and After)

STAGE 2

- No. samples: 18 (from stage 2)
- Measure K_{IC}

STAGE 3

Stage 1

Mode 1 fracture toughness (K_{IC}) is measured for a minimum of 3 SCB samples. These values will provide the baseline K_{IC} value for the particular rock type.

Stage 2

- Stage 2 includes mineralization of SCB discs. The SEM and uCT images will be obtained before and after mineralization experiments to obtain surface and 3D images. .
- Exact experimental conditions to be determined from the results of rate-kinetics tests that are ongoing.

Stage 3

- Mode 1 fracture toughness is determined for all the samples from stage 2 after the CO_2 mineralization.

Pressure / Temperature	500 psia	800psia	1500psia
100ºc	No. samples:3 Data: SEM-EDX, uCT (Before and after)	No. samples:3 Data: SEM-EDX, uCT (Before and after)	No. samples:3 Data: SEM-EDX, uCT (Before and after)
200ºc	No. samples:3 Data: SEM-EDX, uCT (Before and after)	No. samples:3 Data: SEM-EDX, uCT (Before and after)	No. samples:3 Data: SEM-EDX, uCT (Before and after)

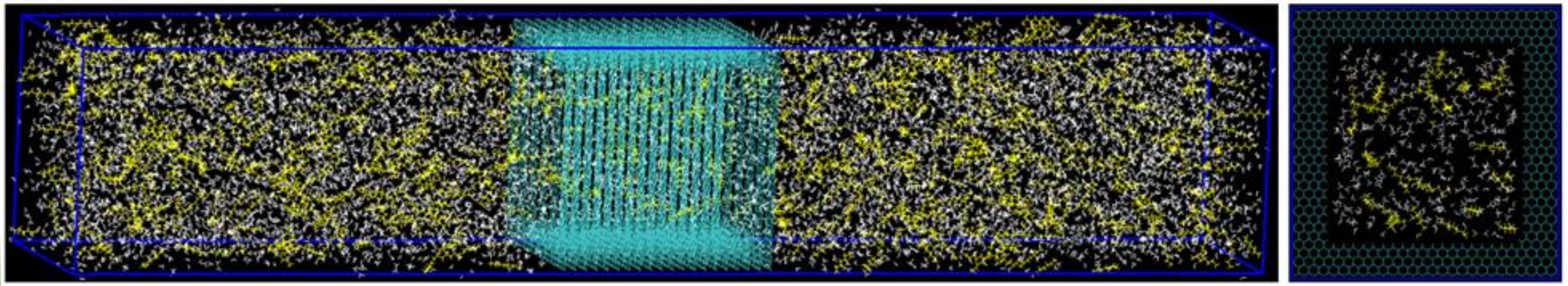
Molecular scale simulation

Our goal: Translation of the characterization results into simplified and quantified physical and chemical processes to develop the large-scale reactive simulation model (next task).

Molecular dynamics simulations to determine:

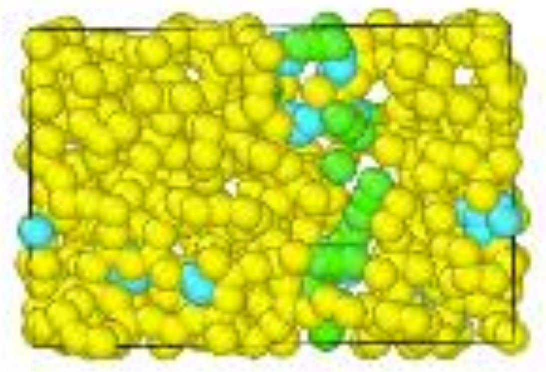
1) If carbon mineralization affect reactive surface area and the reaction rate.
2) If mineralization occurrences uniformly across the rock surface and the pore network
3) Mineralization effect on hydraulic properties, permeability and porosity.

- The results from the molecular dynamics simulations will be integrated with the outcomes of experimental analyses and will be used in the form of analytical expressions and numerical correlations as a feed to the field-scale reactive transport model.



Molecular dynamics simulation model development

Procedures:



- Run simulations and achieve system equilibrium
  - Control temperature, pressure and total energy
  - Conduct simulation for 10ns with the desired temperature and pressure conditions
- Validate model accuracy against experimental and computational studies
- Focus on changes in mineral surface and physical properties

Done:

- Prepared Mg/C/O ReaxFF potential parameters for an all-atom forsterite/water/CO_2 interfacial model
- Implemented ReaxFF, Buckingham, and Lennard-Jones potential for the ionic system

Will do:

- Identify the key reactions between bicarbonate ions and the rock surface.
- Determine the pathways of carbonation reactions and subsequent mineral formation
- Observe the formation of intermediate compounds under various temperature and pressure
- Examine the stability and growth of carbonate minerals on the rock surface.

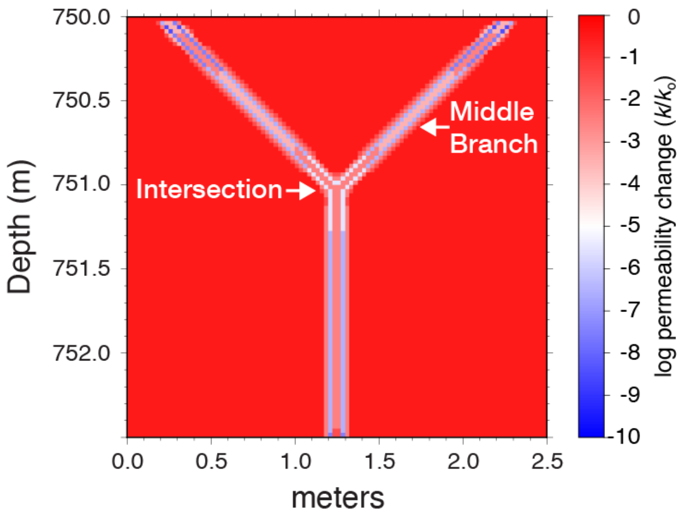
Upscaling and identification of target development areas

In-situ:

- Performing individual reservoir models for sites within the study area to assess *site-scale* carbon mineralization throughout the study area
- Outcome: time-dependent in-situ CO_2 mineralization potential of potential targets throughout the U.S. Mid-Atlantic region.

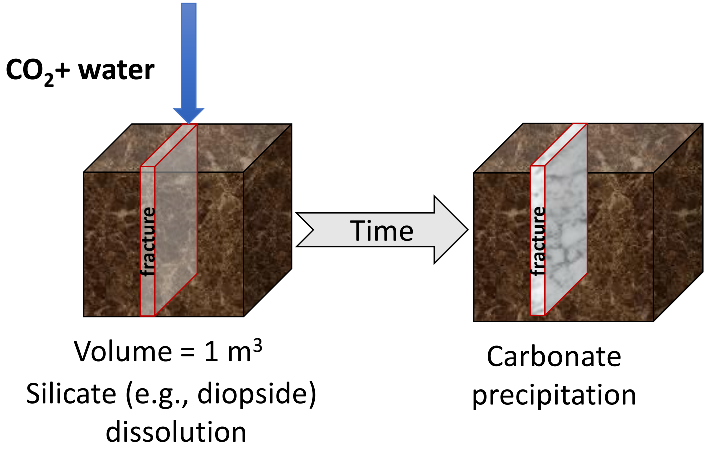
Ex-situ:

- Performing a set of numerical simulations that model flow-through reactor vessels to assess the *ex-situ* carbon mineralization potential for mafic waste rock.
- Outcome: Identification of the optimal fluid chemistry and grain-size distribution, and mineralization efficiency per unit time



permeability change caused by CO_2 mineralization in a basalt fracture

Mixed-flow reactor simulation



Dissolution of CO_2 in aqueous solution (production of acidity):

$CO_{2(g)} + H_2O \rightleftarrows CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$

Dissolution of diopside and precipitation of carbonates:

Diopside dissolution: $CaMgSi_2O_6 + 2H_2O + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_4SiO_4$

Calcite precipitation: $Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+$

Magnesite precipitation: $Mg^{2+} + HCO_3^- \rightarrow MgCO_3 + H^+$

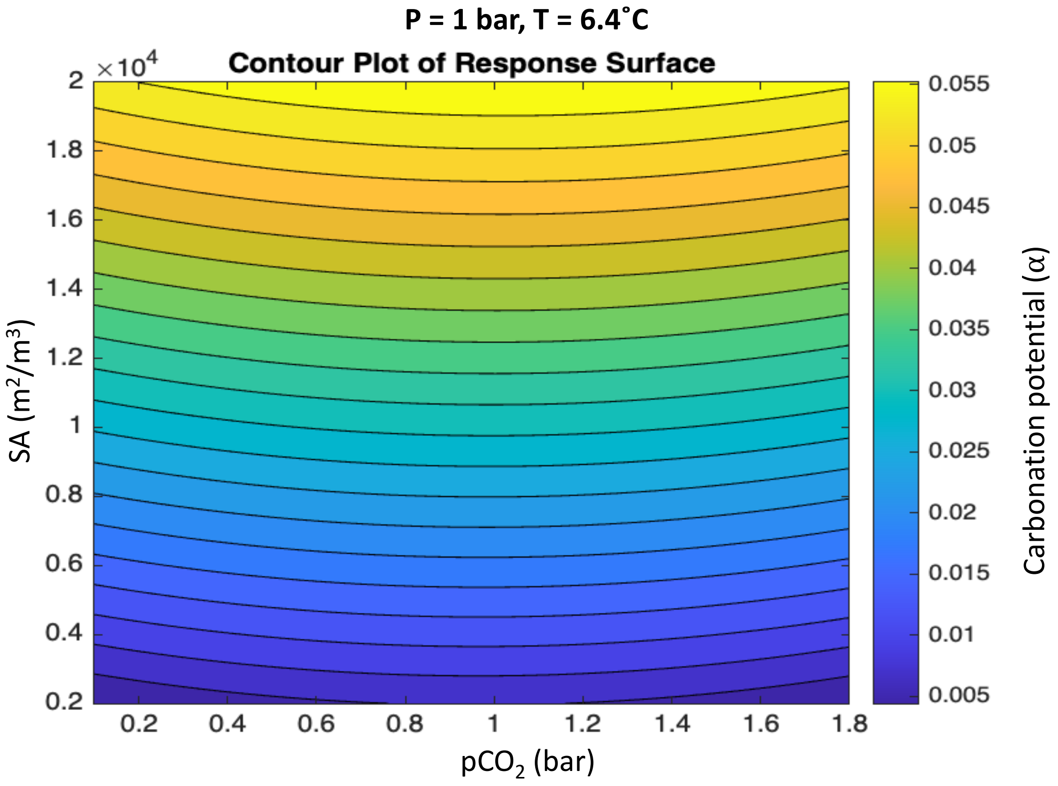
Surface roughness factor (SRF) = $\frac{SA_{total}}{SA_{geom}}$

SA_{geom} = geometric surface area of planer surfaces of the fracture

SA_{total} = reactive surface area of fractured planes considering surface roughness factor

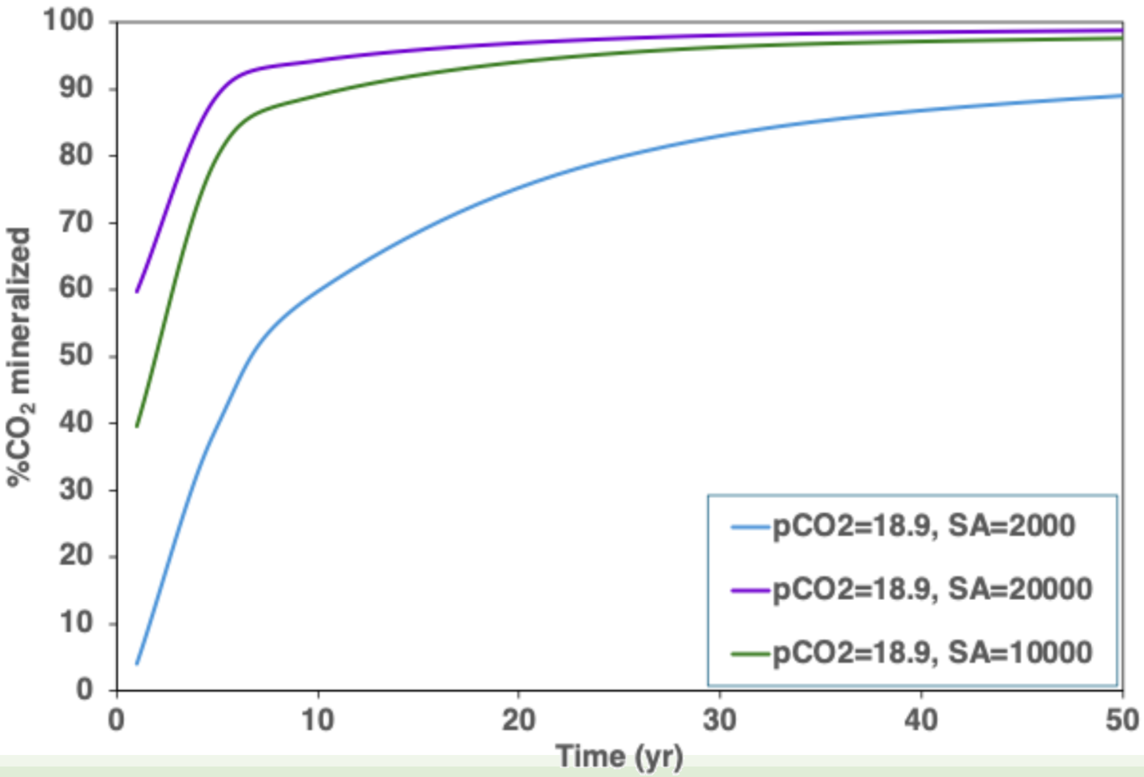
- Mixed-flow reactor with 1m^3 silicate mineral (e.g., diopside) and 1 set of parallel fractures
- Porosity = 2%, Permeability = 10^{-13} m^2, Fracture aperture = 0.001 m
- T = 6.4˚C, P = 1 bar (conservative assumptions for near-surface condition)
- Mineral is reacting with CO_2-rich water through fractures over 1000 years
- Reactive surface area (SA) = 2000 - 20000 m^2/m^3 (variable SRF from 1 to 10)
- Host silicate is dissolving under kinetic constraints, and carbonates are precipitating under equilibrium

Factors controlling carbonation potential of diopside



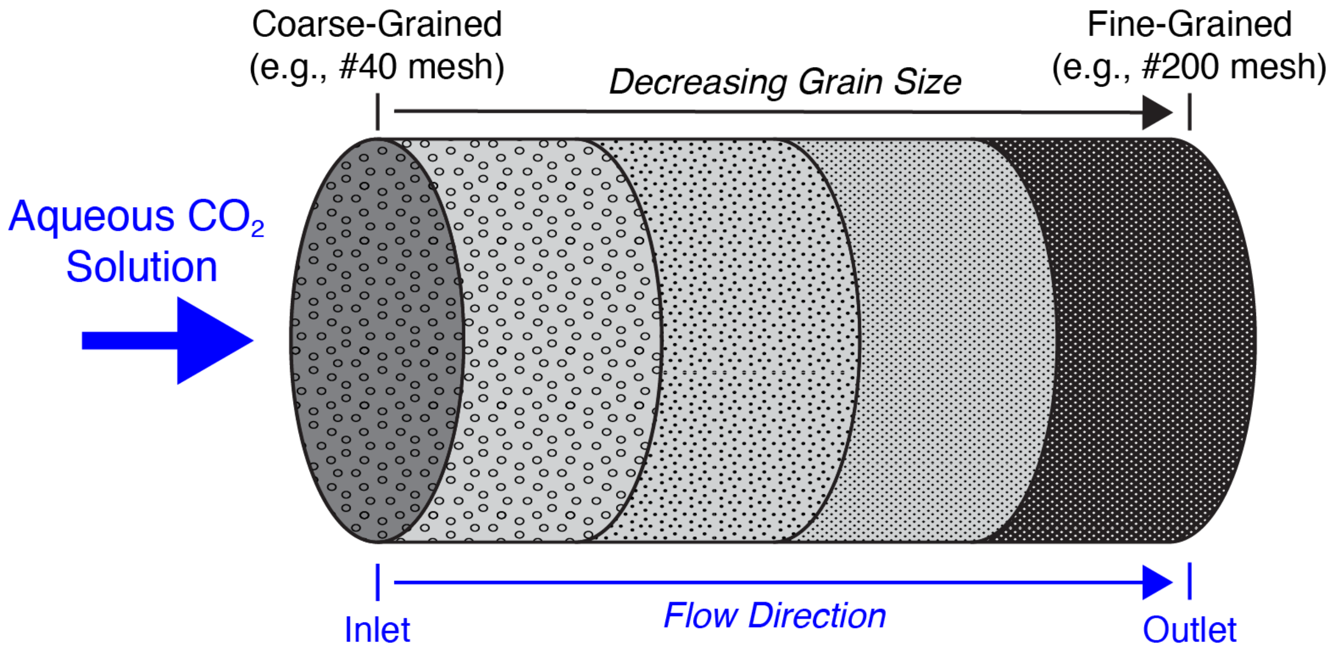
$$\% \ CO_2 \text{ mineralization} = 100 \times \frac{moles\ of\ CO2\ mineralized}{moles\ of\ C\ in\ the\ reactor}$$

$$\text{Carbonation potential } (\alpha) = \frac{g\ of\ CO2\ mineralized}{g\ of\ initial\ diopside\ in\ reactor}$$



- Highly fractured in situ rock or finely-crushed mine wastes with diopside would have high CO_2-mineralization potential.
- >90% CO_2 mineralization occurs <10 years by diopside-rich rocks with highest SA (20000 m^2/m^3).

Next step: Flow-through reactor simulation



- **Design a flow-through reactor containing stacked layers of mafic waste rocks with different grain sizes to optimize CO_2 mineralization efficiency under controlled conditions.**
  - ➢ Systematically decreasing grain size in the direction of flow would provide a higher reactive surface area and a higher residence time of the CO_2-rich water in contact with host minerals, promoting higher carbonation without compromising the reaction efficiency over the long flow path.
- **Test various configurations of this flow-through reactor to identify optimal fluid chemistry and grain size distribution of host minerals to maximize their carbonation potential.**

Ranking, extension to nearby regions, Database development

- Machine learning is used to scan through all the influential factors, to rank the CO_2 mineralization site candidates and locate the most prospective active regions.
- Extension of the resource assessment to the nearby regions with limited geological data, through machine learning regression approaches.
- Development of a map for the Mid-Atlantic region and beyond, by fitting regression models to the predicted storage potentials. (The experiments and reactive transport modeling will be performed for the Mid-Atlantic region.)
- Storage resource data for the Mid-Atlantic areas will be provided to DOE/NETL for inclusion in the Energy Data Exchange (EDX) System.
- High-resolution geologic maps for prioritized locations will be constructed

Future commercialization and mineralization cost assessment

We will assess the cost of mineralization for both potential in-situ and ex-situ resources, and site-specific commercialization plans will be provided by the project team.

In-situ mineralization of CO_2 in geological formations:

- ❑ Proximity to the infrastructure of similar application, e.g. oil and gas wells
- ❑ The potential to extract valuable minerals and critical elements while mineralization

Ex-situ mannerization in mine waste piles and aggregate fines:

- ❑ Earning carbon tax credit (depends on the manner in which CO_2 is disposed or utilized)

Community benefits plan

Appalachia is very rich in terms of natural and geological resources; however, it does experience economic and environmental hardship.

Social and environmental impacts:

- Underserved communities in the Mid-Atlantic region and socio-economic vulnerabilities
- Carbon management and sustainable recovery of unrenewable resources

If these resourceful communities are equipped with a technology to mitigate the environmental issues of resource recovery, their businesses will be better represented and socially more acceptable.

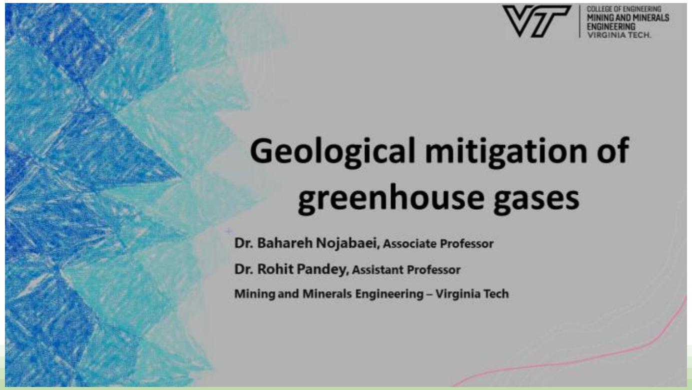
Benefits

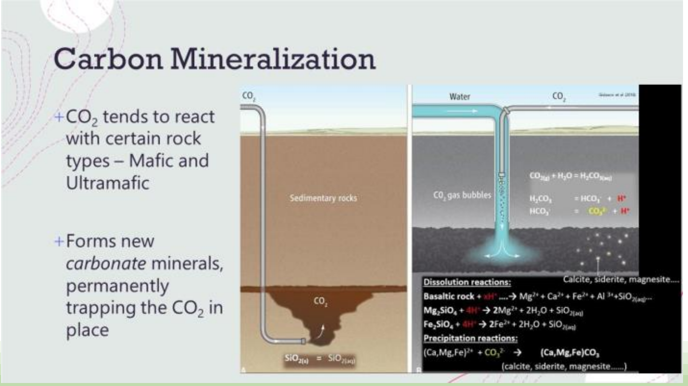
- Job opportunities through making a bridge between the extraction of geological resources and environmental considerations.
- Reaching out to historically underserved groups, high schools, and colleges within the US Mid-Atlantic region, and communicate the goals of the project with them.
- Facilitating visits to the Virginia Tech Blacksburg campus

Diversity, equity, inclusion, and accessibility (DEIA) Overview

- Encouraging people from underrepresented in STEM groups to join our projects.
- Attending workshops and trainings which target implicit bios and promotes equity and inclusion.
- SWAM participation for materials and supplies
- Collaborating with CEED and other existing programs that promote diversity and inclusion within Virginia Tech.

C-Tech² program is designed and intended for rising junior and senior high school girls.
The goal is to expose students to the broad range of engineering disciplines.





Project timeline

Task Name	Assigned Resources	Year 1				Year 2			
		Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Task 1.0 – Project Management and Planning	B. Nojabaei and N. Ripepi, VT								
Task 2.0 – Task 2.0 - Geological Assessment	VaDOE & VT								
Subtask 2.1 – Geologic overview	VaDOE	A							
Subtask 2.2 – Pre-field Study mapping	VaDOE		B						
Subtask 2.3 – Suitable industrial waste sites investigation	VaDOE & VT	C							
Task 3.0 - Prospective CO2 Storage Resource Characterization	VT								
Subtask 3.1 – Laboratory analyses of rock physical properties	R. Pandey, VT					D			
Subtask 3.2 – Laboratory Analyses of reactions and product evaluation	Wencai Zhang, VT					E			
Subtask 3.3 – Molecular scale simulation	B. Nojabaei, VT					F			
Subtask 3.4 – Upscaling and identification of target development areas	R. Pollyea, VT						G		
Task 4.0 – Post-Field Study Mapping	VaDOE & VT								
Subtask 4.1 – Ranking targets through using machine learning	B. Nojabaei, VT							H	
Subtask 4.2 – Database development for potential site candidates	VaDOE								I
Subtask 4.3 – Data analyses and extension to nearby regions	B. Nojabaei, VT								J
Task 5.0 – Future Commercialization and Mineralization Cost Assessment	B. Nojabaei and N. Ripepi, VT								K

Project benefits

- The resource assessment and characterization of mineralization sites in the U.S. Mid-Atlantic **empowers businesses to lead this carbon management effort** in regional and global scales.
- To help the U.S. achieve its climate and environmental ambitions, these procedures should be **cost-effective**. Throughout this project, we provide insight on how to proceed with the most suitable mineralization **approach and location**, that is not only environmentally viable, but also is it **economic in long term**.
- In addition to carbon storage capacity assessment, the **extractability of critical elements** will be evaluated. This will contribute to the development of concurrent carbon mineralization and critical elements recovery strategies in the future.

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