Targeted Mineral Carbonation to Enhance Wellbore Integrity

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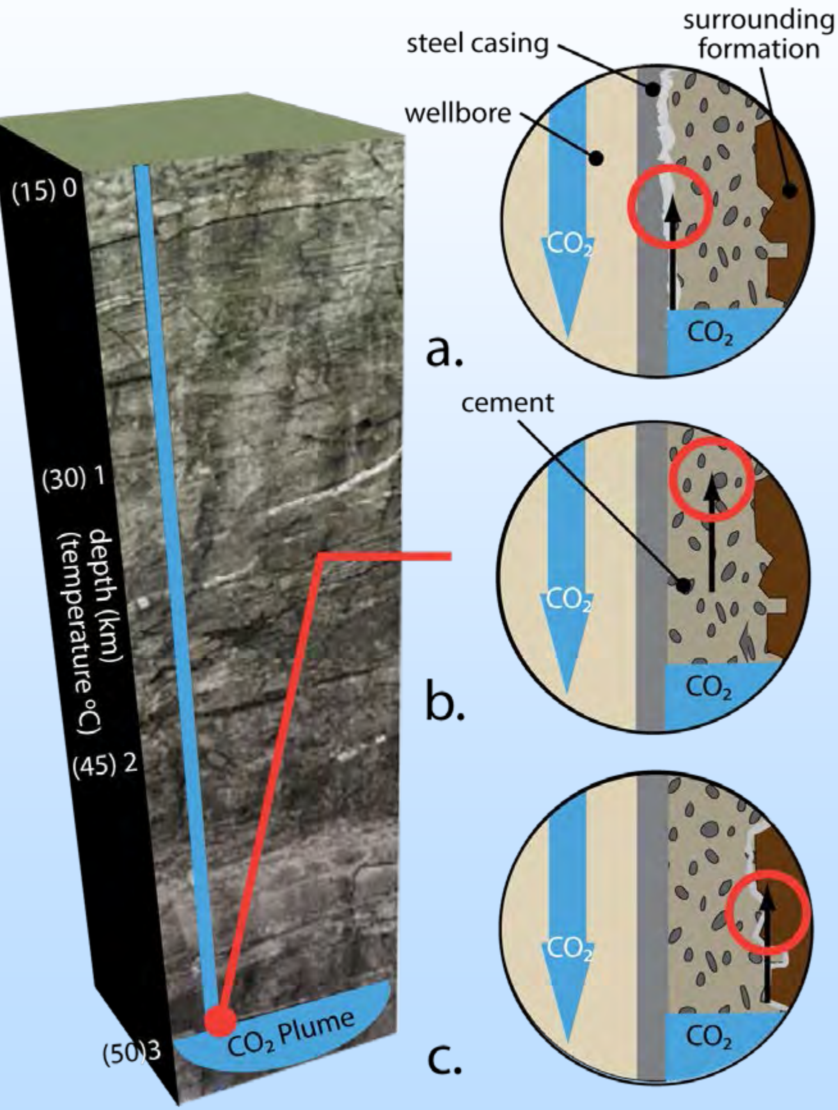
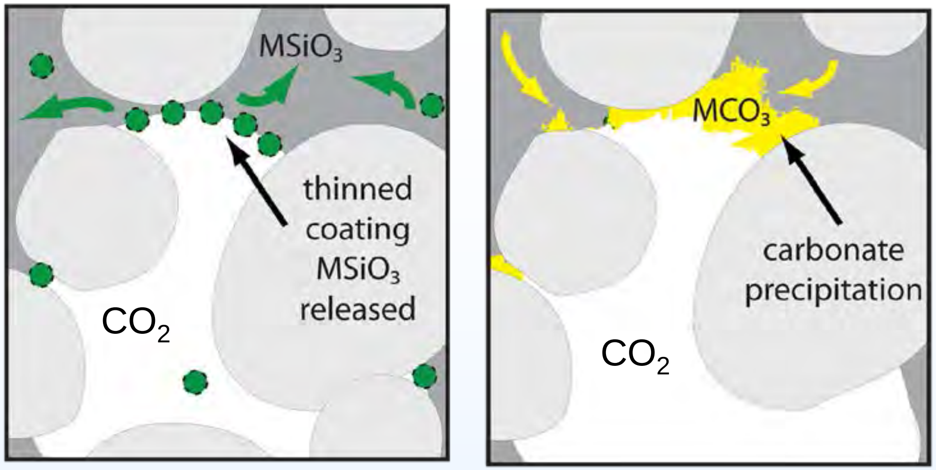
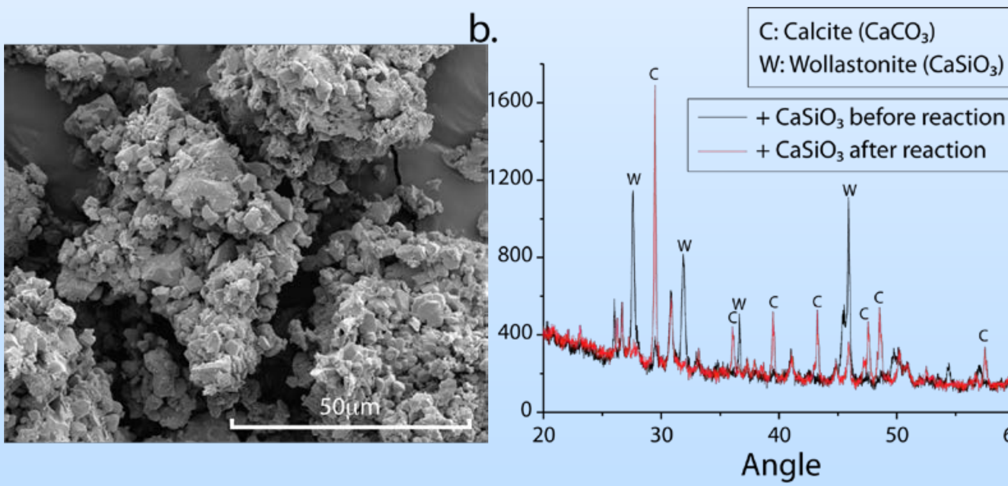
Carbon mineralization for permeability reduction





$$CaSiO_{3(s)} + 2H^+ \leftrightharpoons Ca^{2+} + SiO_{2(am)} + H_2O$$

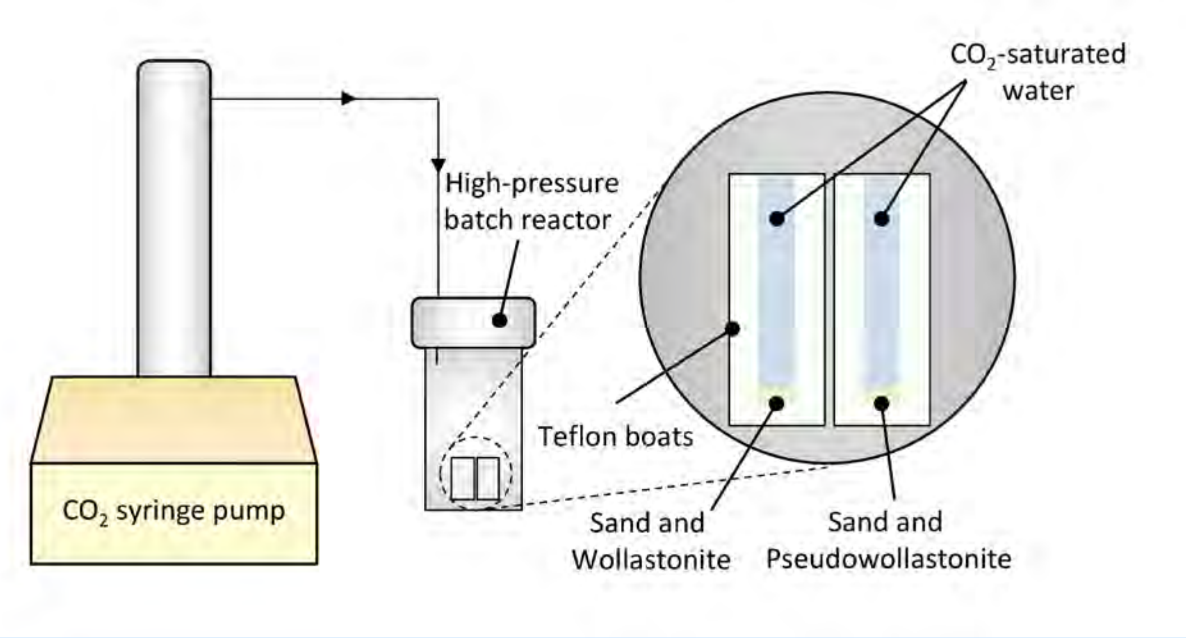
$$Ca^{2+} + CO_{2(aq)} + H_2O \leftrightharpoons CaCO_{3(s)} + 2H^+$$



Tao, et al. (2016), Env. Eng. Sci., 10/16

Batch reaction experiments

Wollastonite and pseudowollastonite were prepared using citrate-nitrate gel auto-combustion to make a calcium silicate ash that was calcined at ~1000 deg C.



150±3°C.
15.5MPa.
24 hours

Analytical methods:

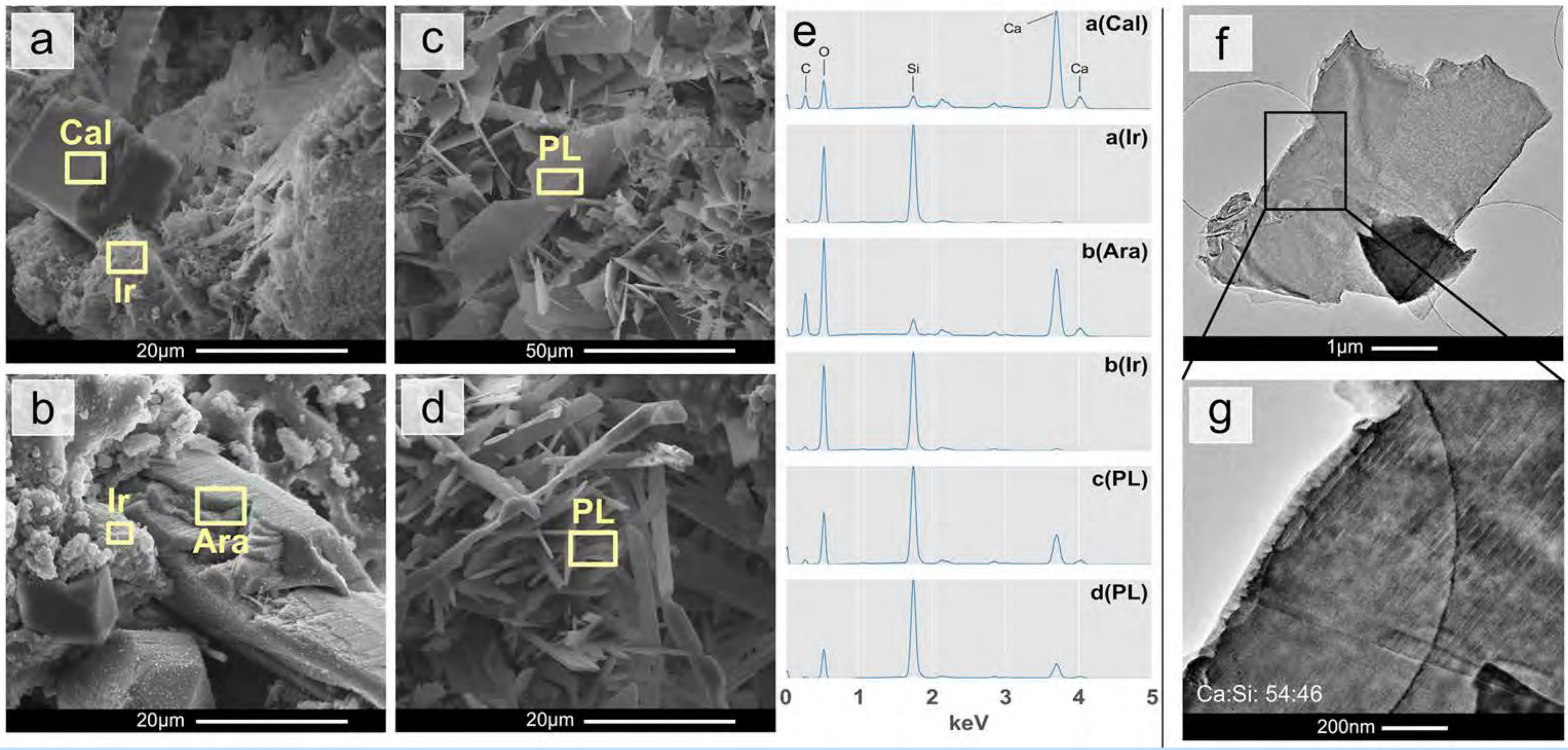
- SEM-EDS for morphology and elemental composition.
- Powder XRD for bulk analysis of reaction produces.
- TEM selected-area electron diffraction (SAED) for single particles.
- ICP-OES to analyze aqueous phases.

Reacting with $CO_{2(aq)}$ …

wollastonite (a) yields only calcium carbonate

pseudowollastonite (b-d) yields calcium carbonate and plate-like calcium silicate hydrate phases

Single particle TEM selected area electron diffraction (SAED)



Calcium silicate crystal structure impacts reactivity with CO_2 and precipitate chemistry

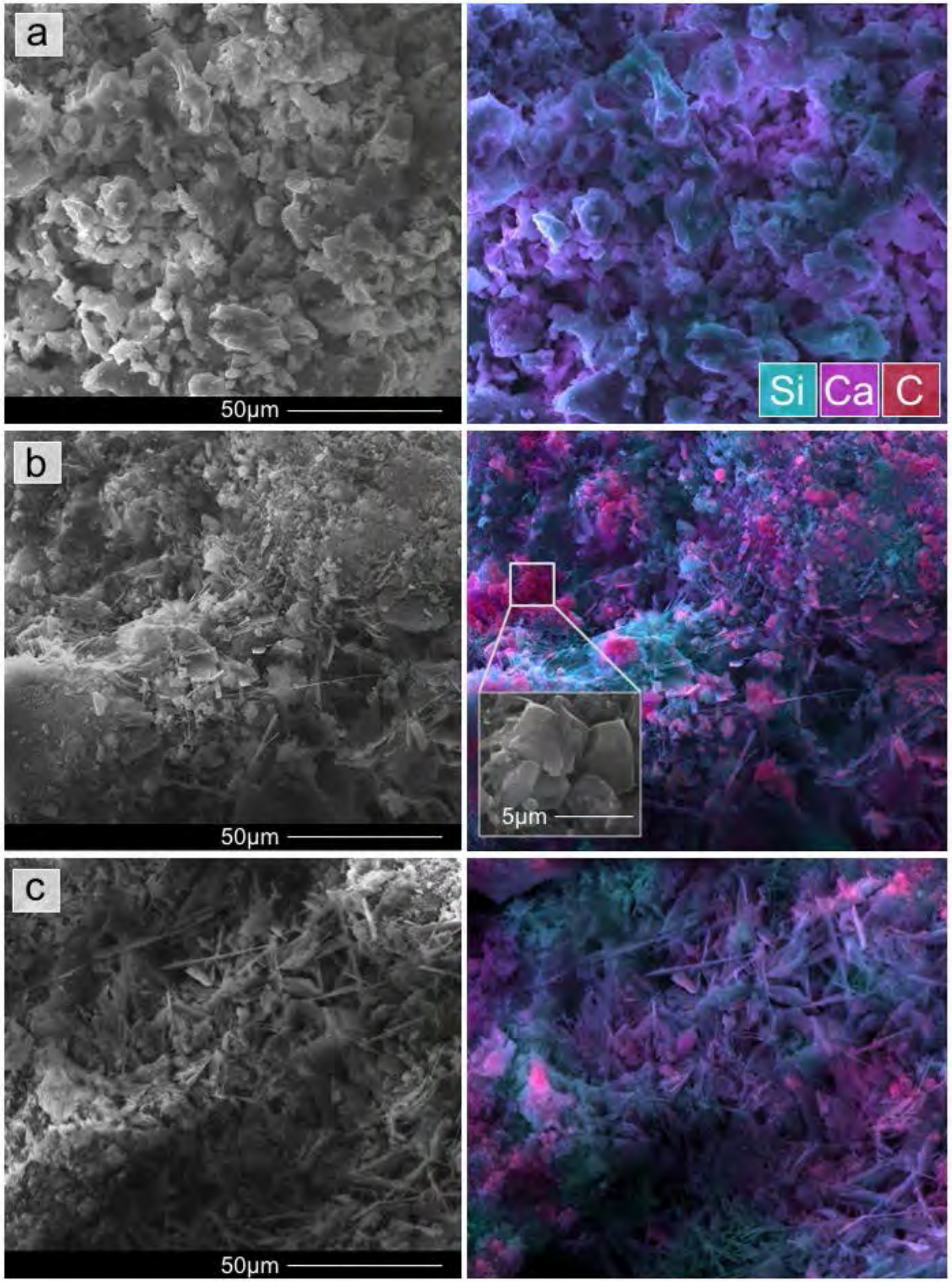
Plattenberger et al. (2018) ES&T Letters. *Under review*

The plate-like phases are more resistant to acid dissolution (pH 5.5 acetic acid)

(a) unreacted $CaSiO_3$

(b) reacted showing $CaCO_3$ and plate phases

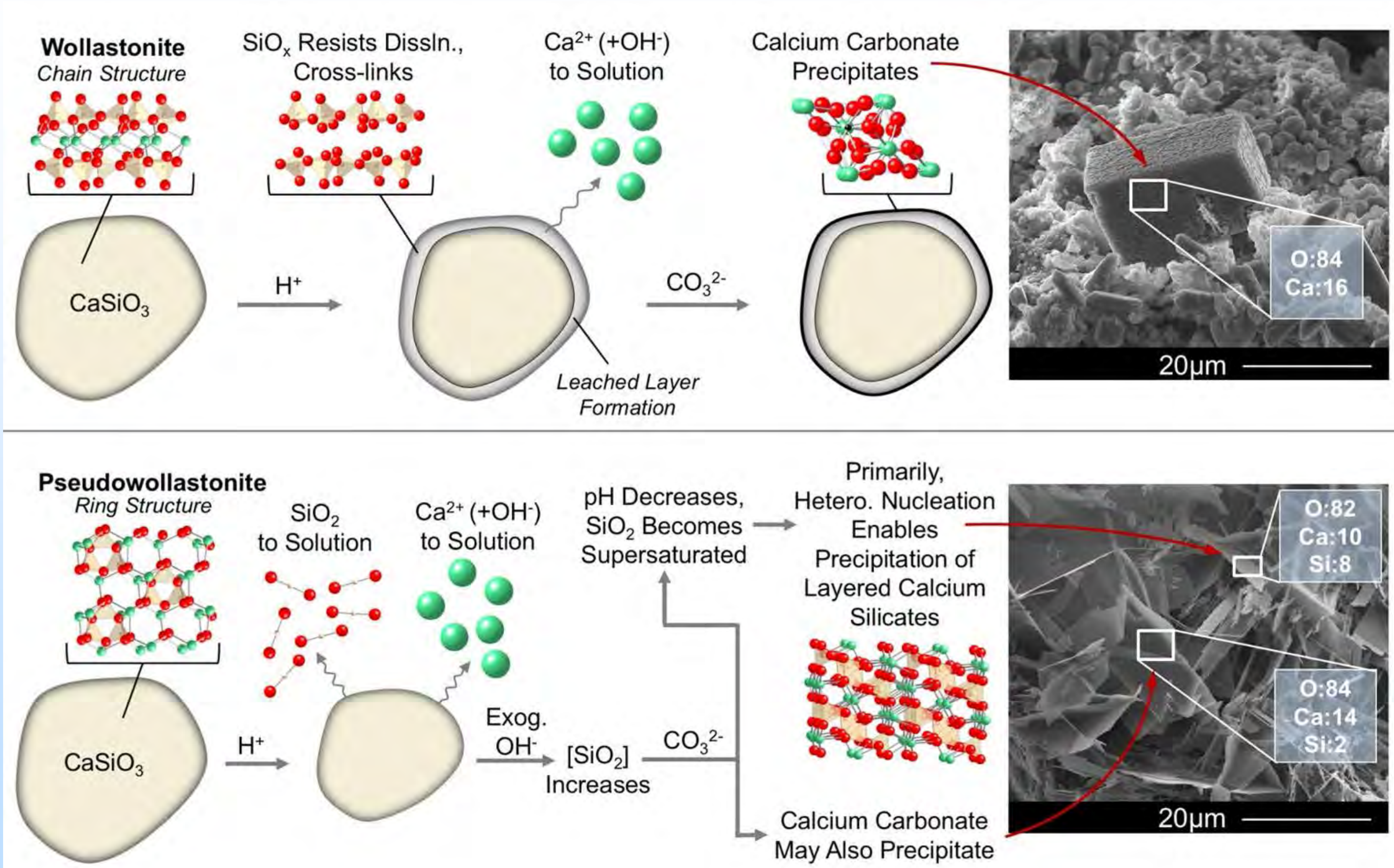
(c) after acid washing showing, only plate-like silicate phases remain



Calcium silicate crystal structure impacts reactivity with CO_2 and precipitate chemistry

Plattenberger et al. (2018) ES&T Letters. *Under review*

A proposed mechanism to explain the difference between the polymorphs



Calcium silicate crystal structure impacts reactivity with CO_2 and precipitate chemistry

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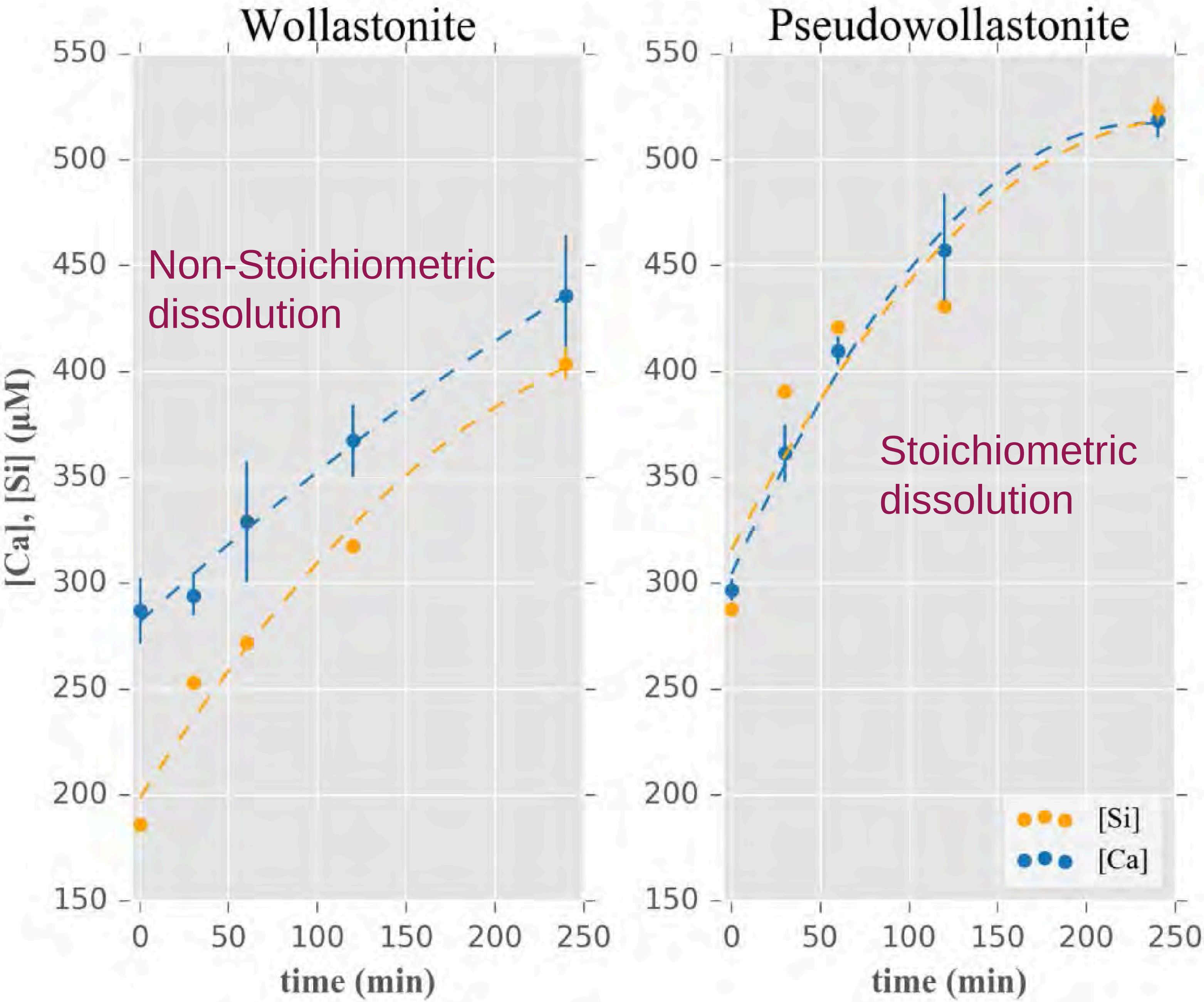
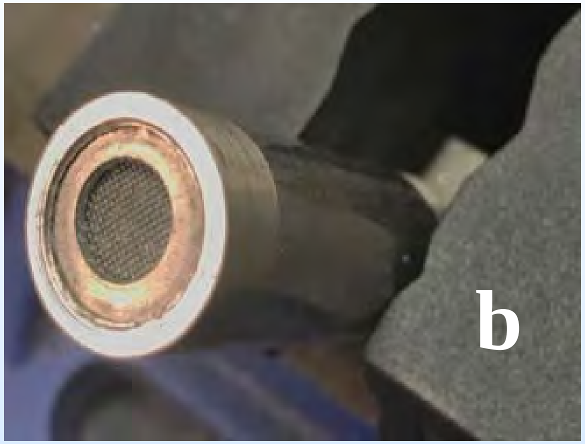


Calcium silicate crystal structure impacts reactivity with CO_2 and precipitate chemistry
Plattenberger et al. (2018) ES&T Letters. *Under review*

Implications for Permeability Reduction – column experiments with pseudowollastonite

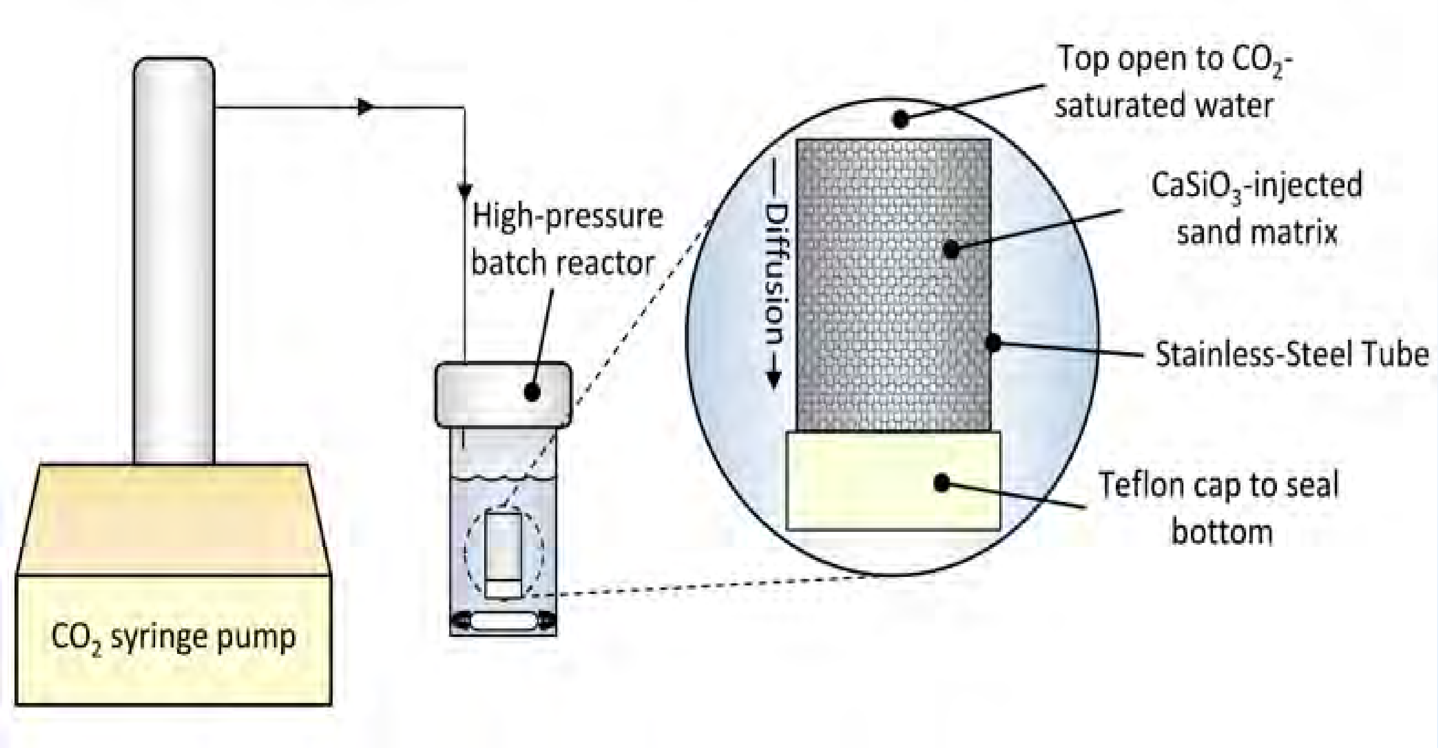
(a) PseudoWollastonite, suspended in water, is injected at high pressure into sand-packed columns in a custom-machined holder.

(b) On each end of the columns are stainless-steel washers and mesh.



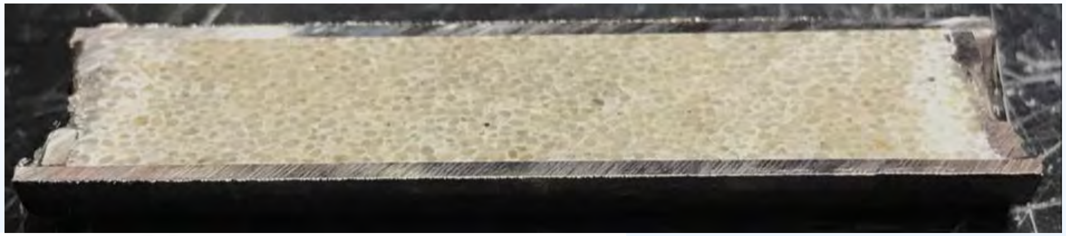
(c) After injection, an even distribution of PWol along the length of the columns is observed.

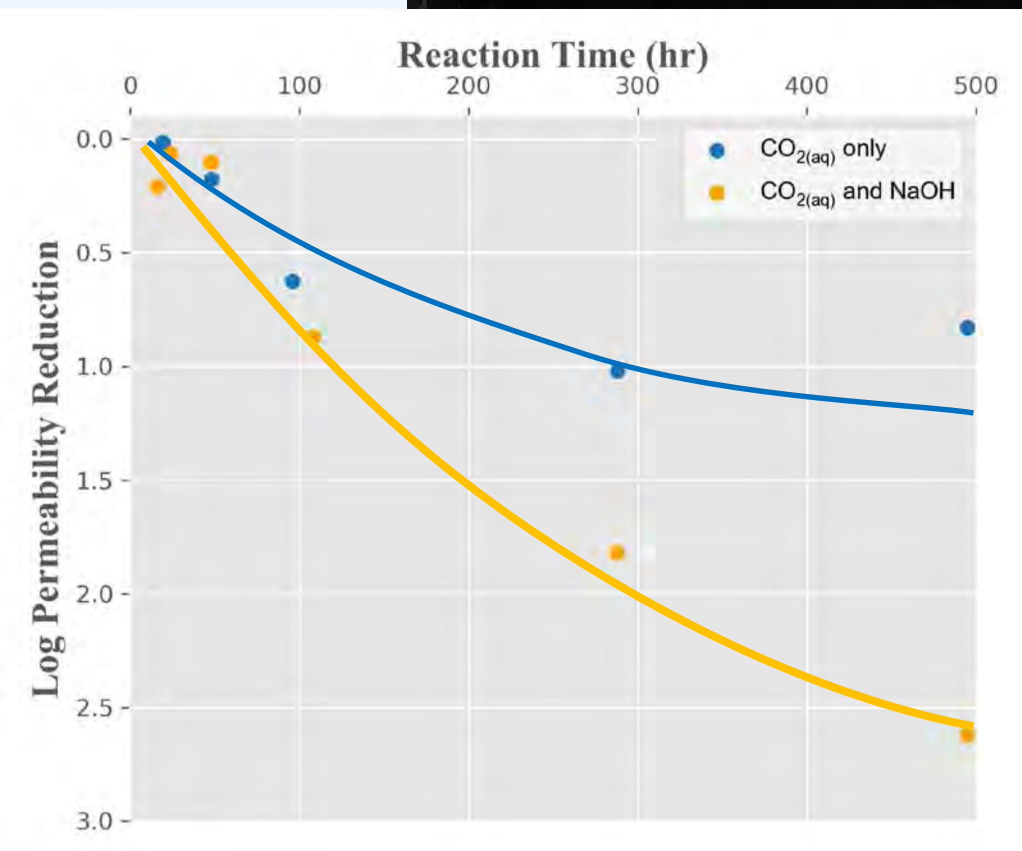
Implications for Permeability Reduction – column experiments with pseudowollastonite



CO_2 is injected into the headspace of a pressure vessel where it dissolves into the aqueous phase and diffuses through the sand/PWol columns. The bottom end of the columns is sealed.

Implications for Permeability Reduction – column experiments with pseudowollastonite

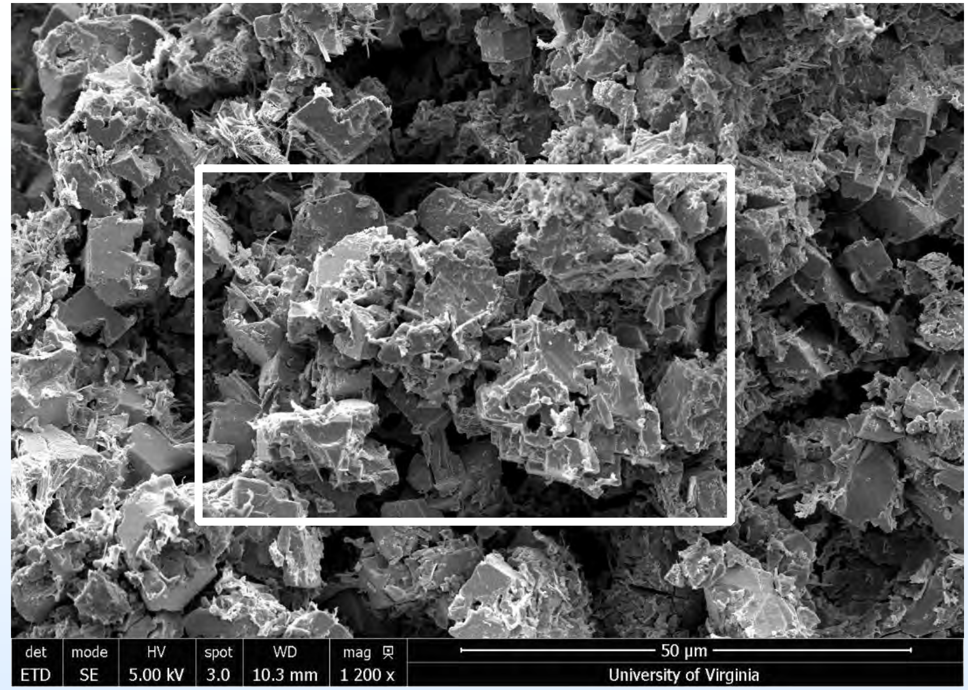


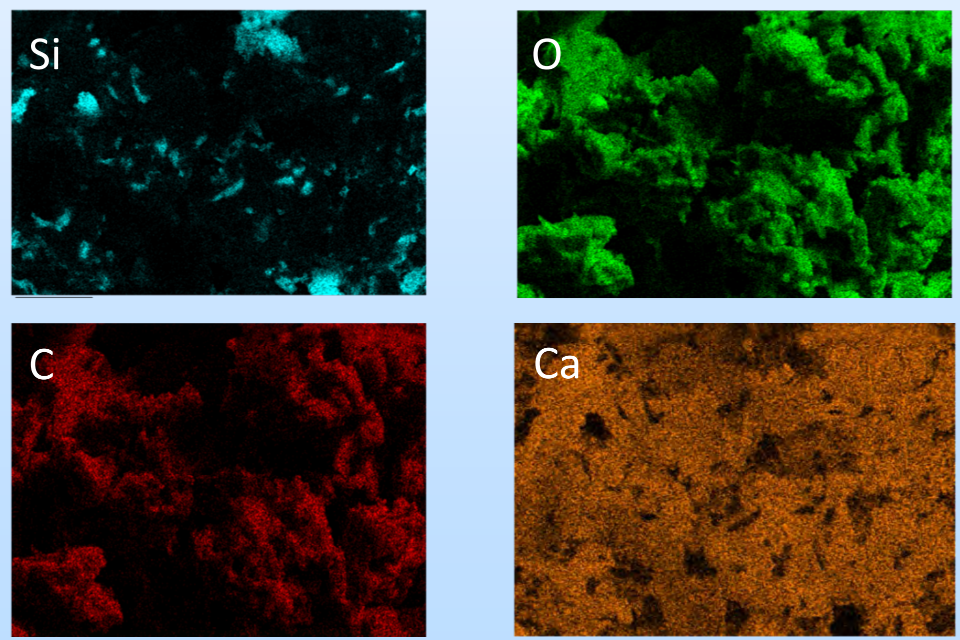


Order-of-magnitude decreases in the permeability of the columns.

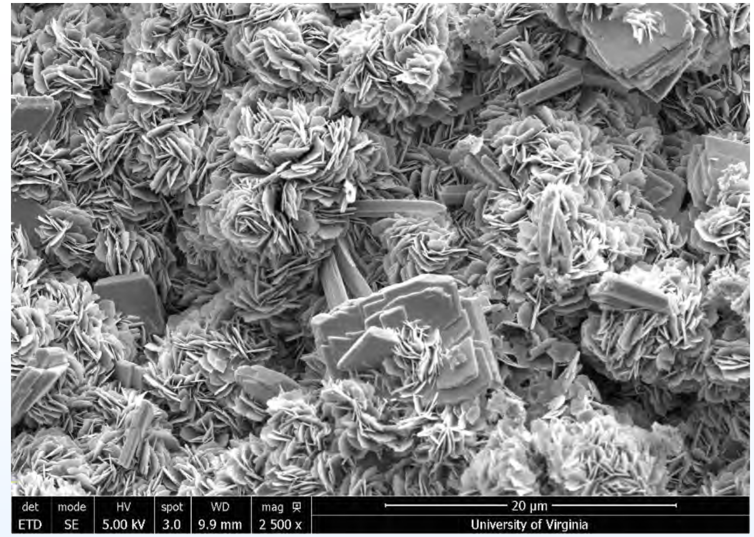
Slight increase in pH increases permeability reduction.

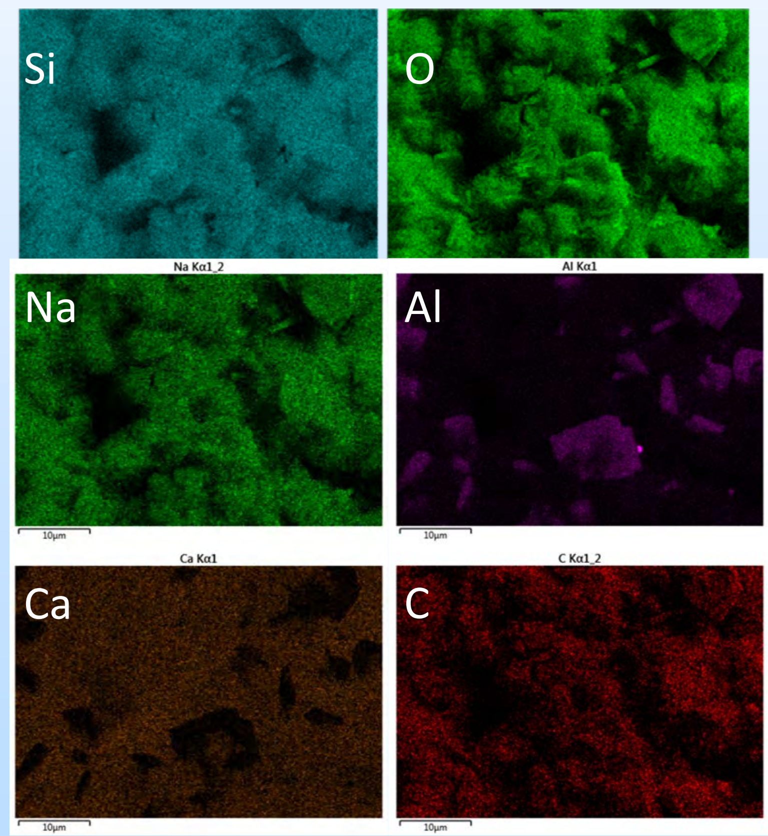
Diffusion


det
mode
HV
spot
WD
mag
ETD
SE
5.00 kV
3.0
10.3 mm
1 200 x
50 µm
University of Virginia


Si
O
C
Ca

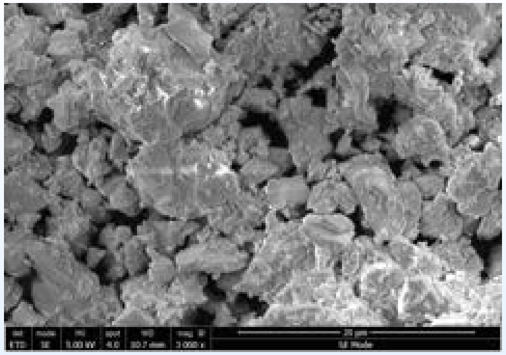
Diffusion

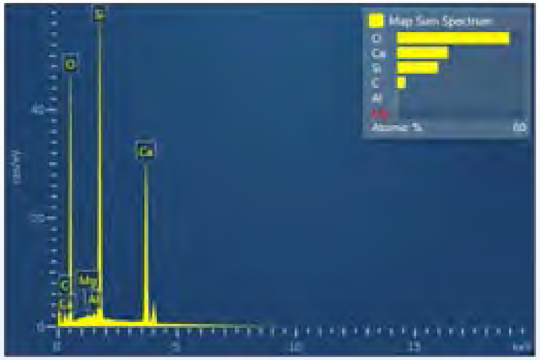

det mode HV spot WD mag
ETD SE 5.00 kV 3.0 9.9 mm 2 500 x
20 µm
University of Virginia


Si
O
Na Kα1_2
Na
Al Kα1
Al
Ca Kα1
Ca
C Kα1_2
C
10µm

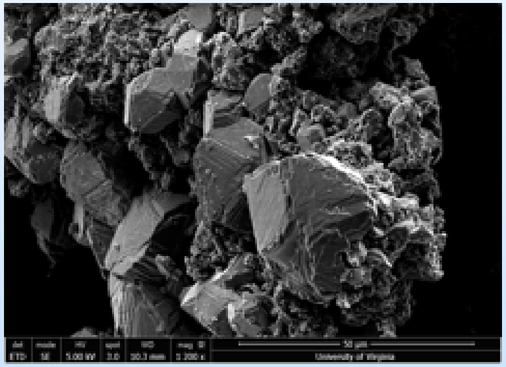
complex reaction pathway

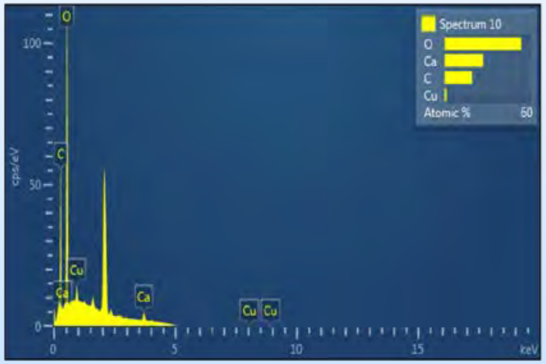
Unreacted
Pseudowollastonite



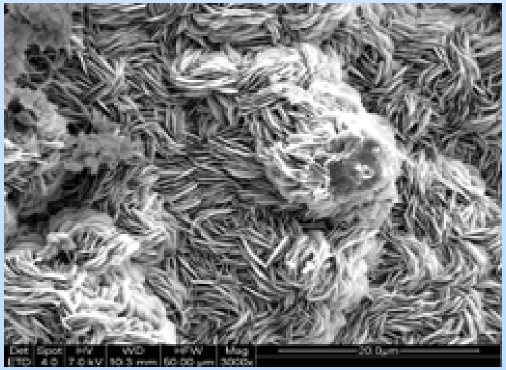


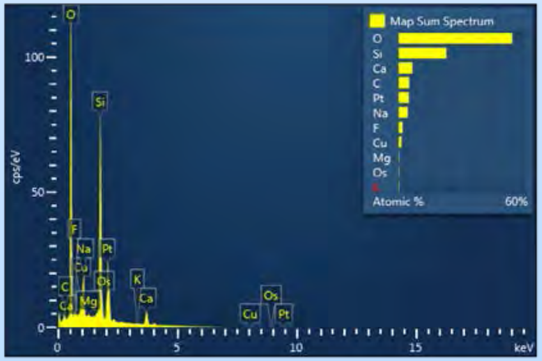
Calcium
Carbonate



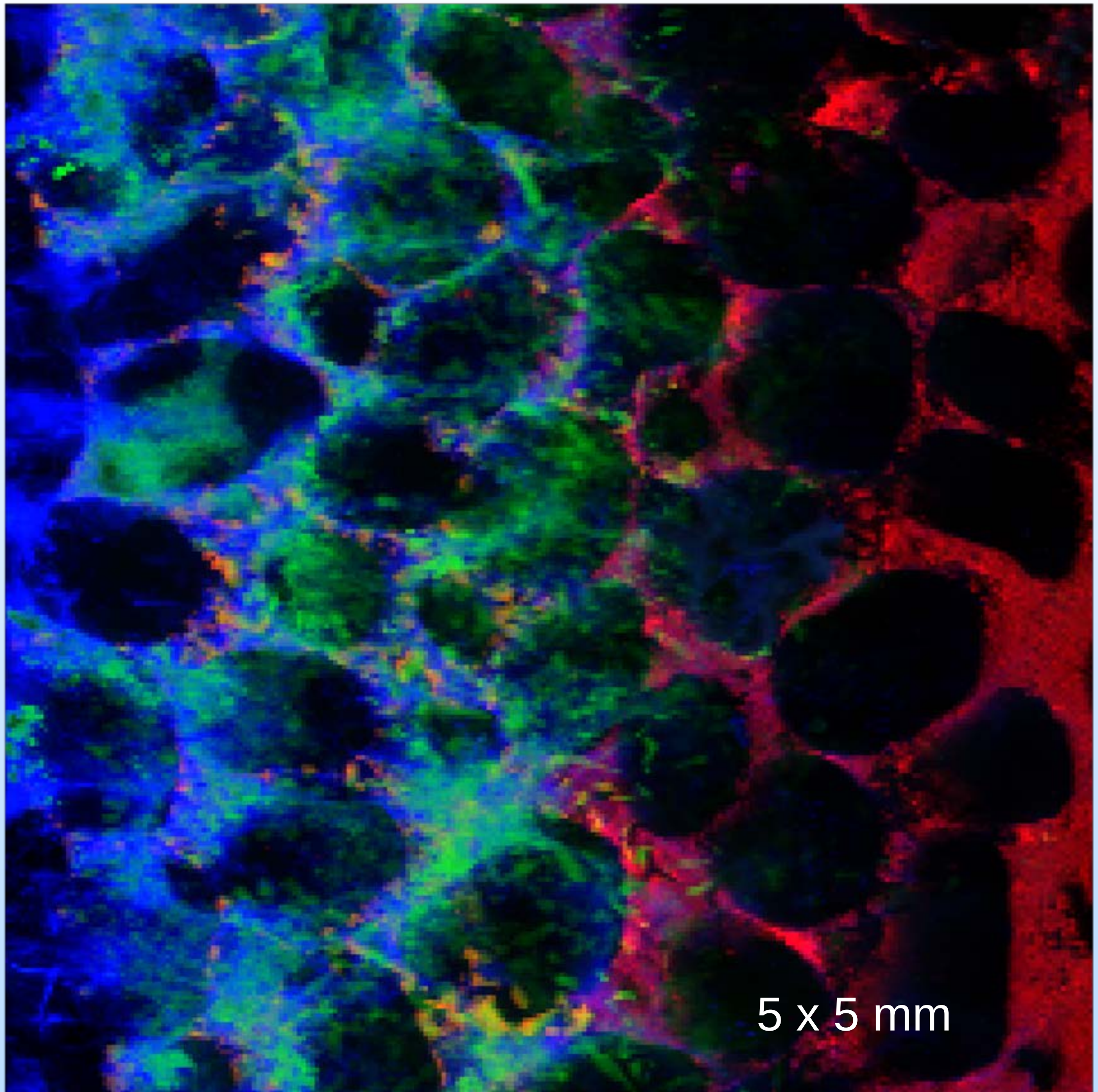


O-Si-Ca-C
Phase





XRF Elemental maps - X-ray microprobe (13ID-E, APS, Argonne Natl Lab)



Columns were reacted for 96hr.

- Sr was added as a reactant to incorporate into carbonate phases, substituting for Ca.
- Post reaction submersion in NaBr solution, as a tracer for water accessibility.

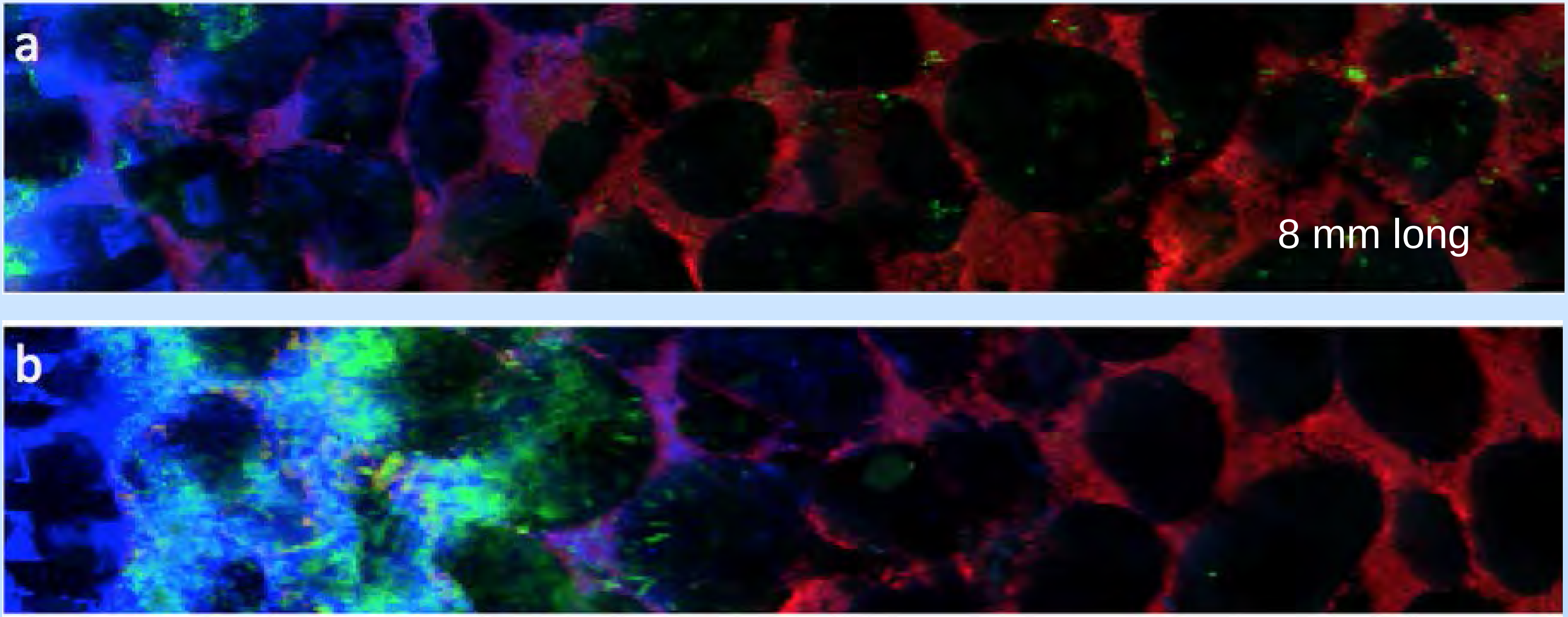
Blue: Br | Green: Sr | Red: Ca

XRF Elemental maps - X-ray microprobe (13ID-E, APS, Argonne Natl Lab)

Columns were reacted for 96hr, then submerged in NaBr solution

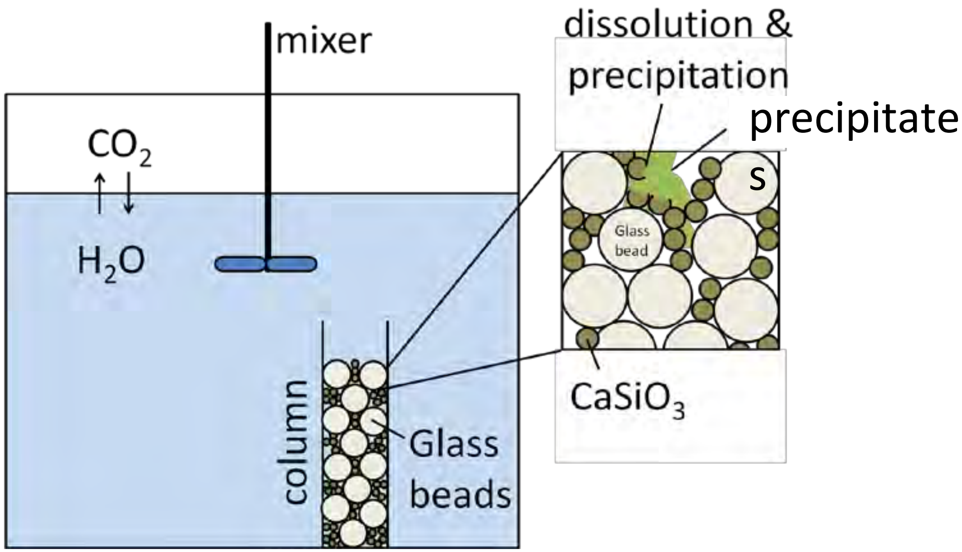
a: NaOH and CO_2 - minimal $CaCO_3$ precipitation and Br diff.

b: CO_2 only - significant $CaCO_3$ and deeper Br diff.



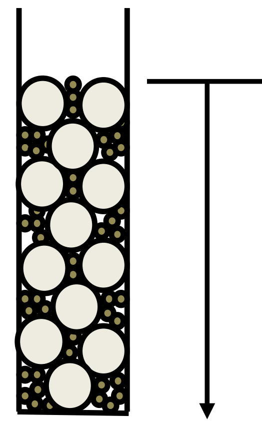
Blue: Br | Green: Sr | Red: Ca

1D Reactive Transport Geochemical Modeling



Giammar et al. (2013)

Transport



C, Ca, Si Diffusion

$$\frac{\partial(C\Phi)}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial C}{\partial x}\Phi\right)$$

C = concentration
ϕ = porosity
D = diffusion coefficient

$CaSiO_3$ filled glass bead columns placed in high P, high T vessel and filled with pre-boiled H_2O

- 160 psi
- Temperature = 90° to 150°C
- Reaction time: 0 – 96 hrs

Dissolution & Precipitation Reactions

$$CaSiO_{3(s)} + 2H^+ \leftrightarrow Ca^{2+} + SiO_{2(aq)} + H_2O$$

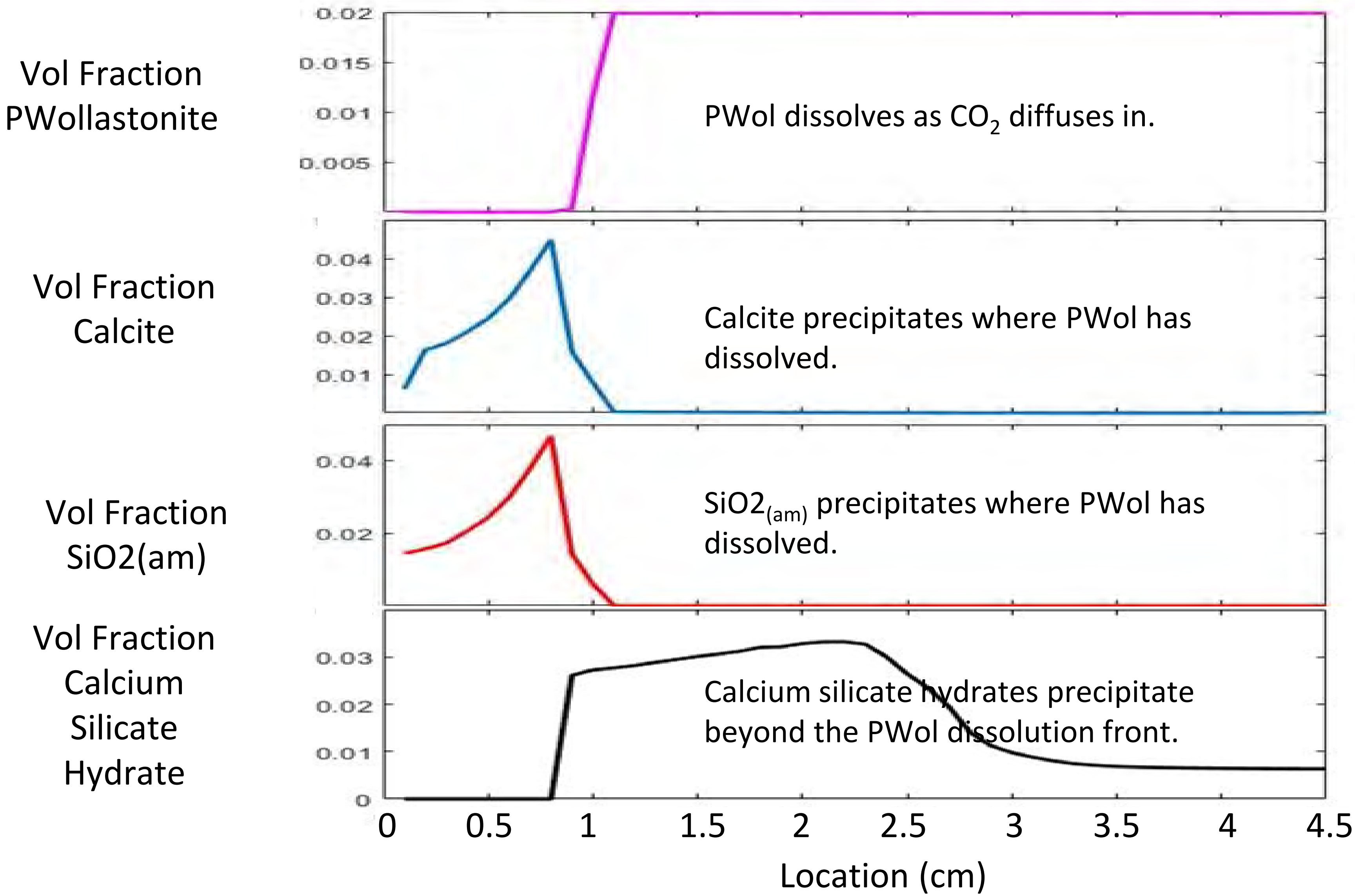
$$CaCO_{3(s)} \leftrightarrow Ca^{2+} + CO_3^{2-}$$

$$SiO_{2(aq)} \leftrightarrow SiO_{2(am)}$$

$$Ca_5Si_6H_{11}O_{22.5} + 10H^+ \leftrightarrow 5Ca^{2+} + 6SiO_{2(aq)}$$

1D Reactive Transport Modeling Results

Precipitation Fronts – 11 hrs of Reaction



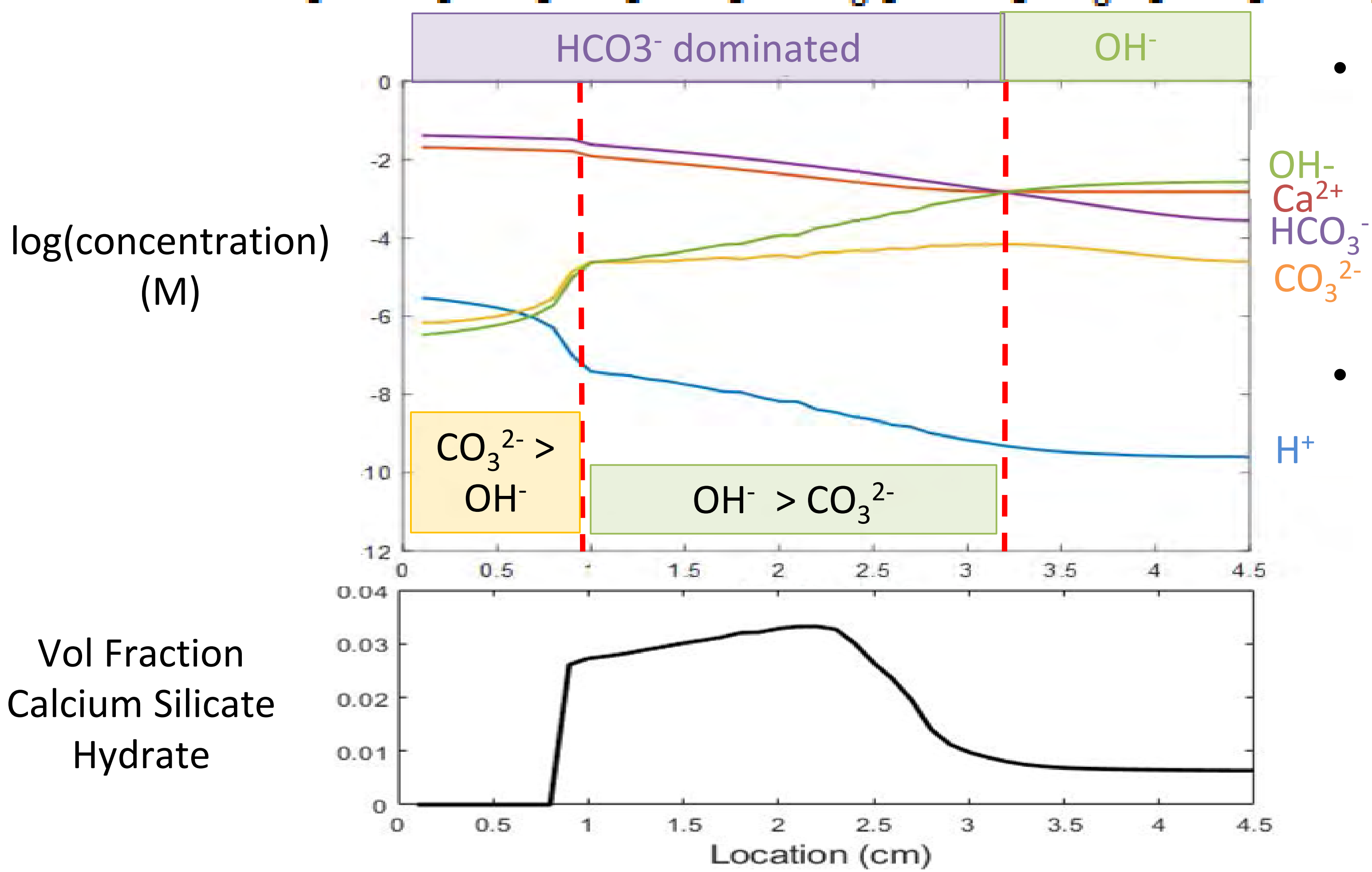
1D Reactive Transport Modeling Results

Calcium Silicate Hydrate Formation

What controls pH?

Conservation of charge:

$$2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$



- Ca^{2+} is always the dominant cation
- The dominant anions from the extent of CO_2 diffusion define the 3 regimes of calcium silicate hydrate precipitation

Summary

- Pseudowollastonite reacts with CO_2 to precipitate acid-stable calcium silicate hydrates. Wollastonite only forms calcium carbonates.
  - Mechanism: Pseudowollastonite undergoes stoichiometric dissolution, saturating the solution with silicate in addition to Ca^{2+}.
- The plate-like calcium silicate hydrates are more acid resistant than carbonate phases.
  - Engineered systems that promote these precipitates are promising for permeability reduction for reliable fluid containment.
- Deployment in porous media requires creation of zones of ideal geochemical conditions (pH, etc.).

many thanks

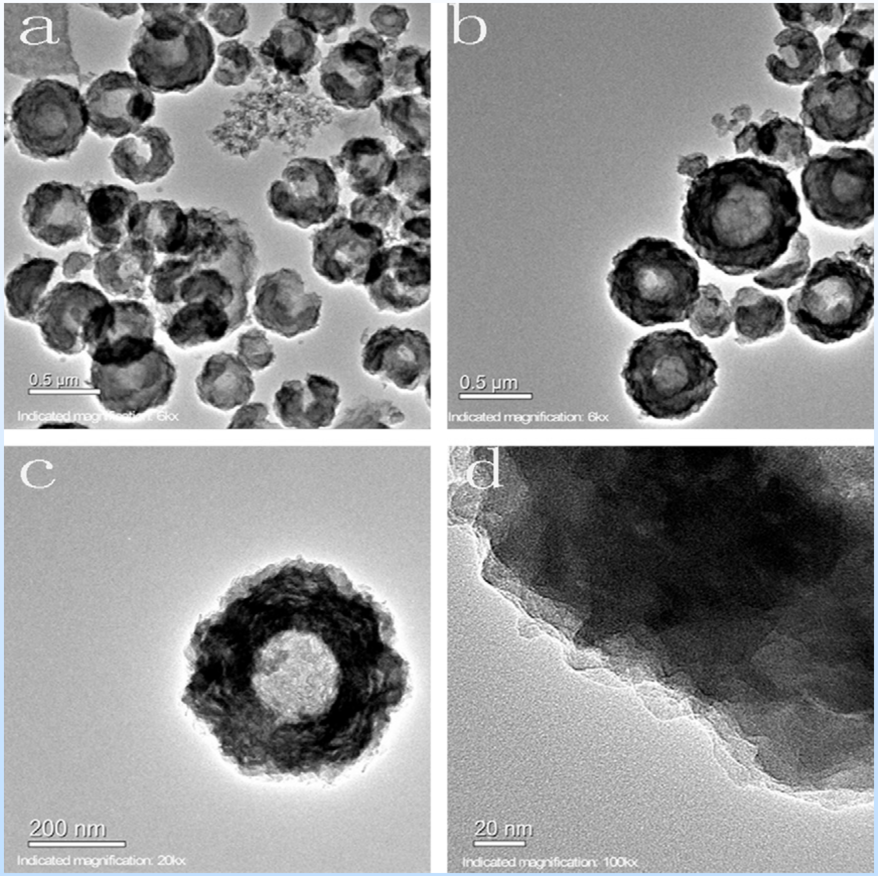
Extra slides

PDMAEMA polymer coating

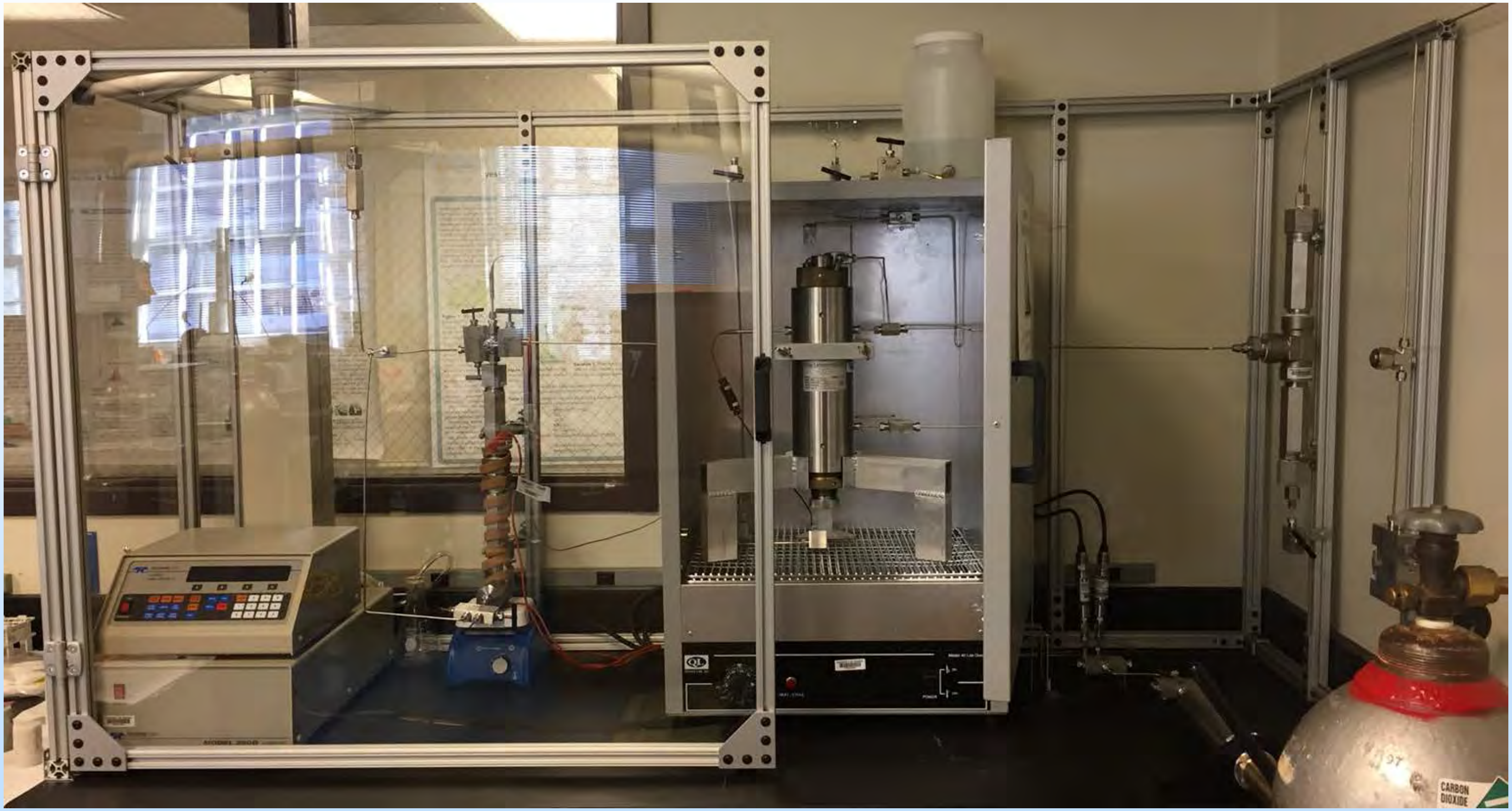
- LCST: vary from 14 to 50℃ in pure water (46℃ in pH 7 buffer)

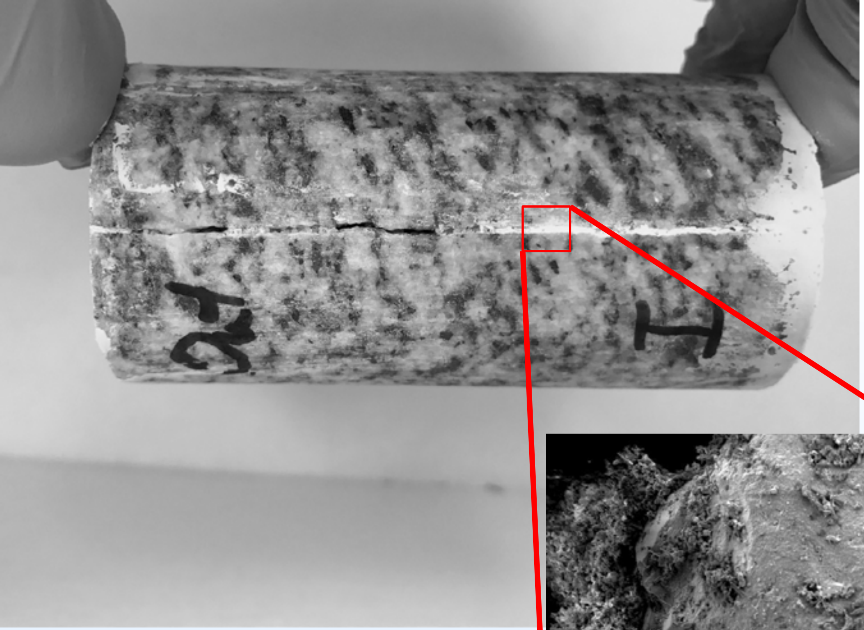
- Coating: surface-initiated atom transfer radical polymerization (SI-ATRP) on the surface of wollastonite nanoparticles

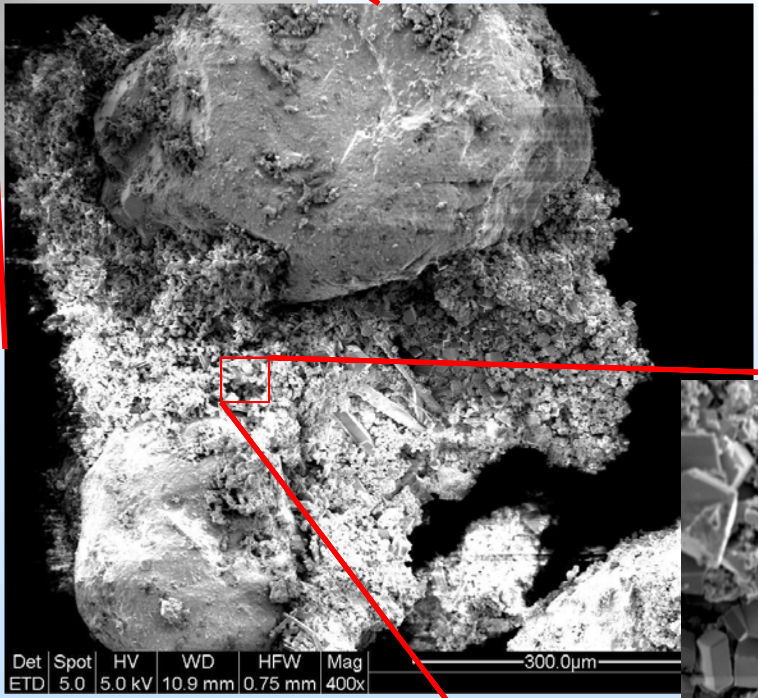
- pH responsive: phase transition and solving/collapsing under low pH condition.

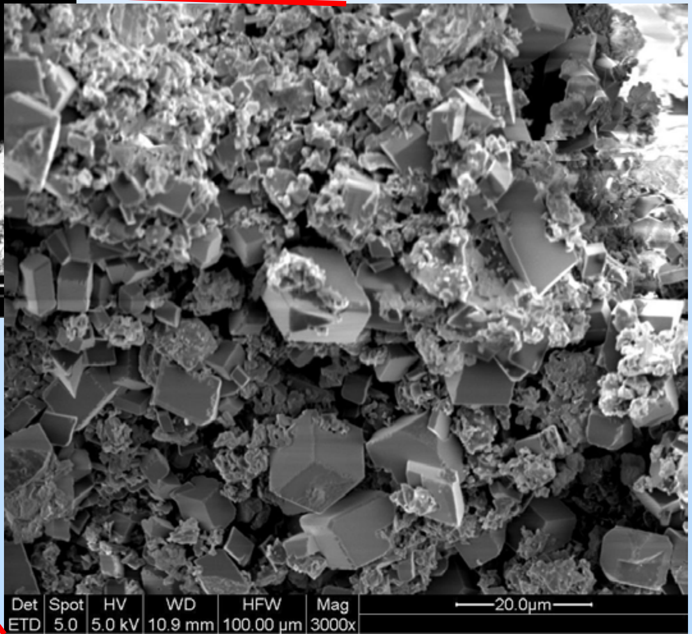


fracture test-rig






Det ETD
Spot 5.0
HV 5.0 kV
WD 10.9 mm
HFW 0.75 mm
Mag 400x
300.0μm


Det ETD
Spot 5.0
HV 5.0 kV
WD 10.9 mm
HFW 100.00 μm
Mag 3000x
20.0μm

benefit to the program

- Program goals
  - >99% storage permanence
  - predict storage capacity to +/-30%
  - improve storage efficiency.
- Project benefits: This project will produce new materials and a novel method to seal leakage pathways that transect the primary caprock seal and are associated with active injection, extraction or monitoring wells (e.g., wellbore casing and cement, and proximal caprock matrix)

project overview: goals and objectives

- Project management and planning
- Coated silicate development, characterization and interaction in porous media
  - Fluid mixing and buoyancy experiments at formation T/P to optimize material properties
  - Evaluate the performance of coated mineral silicates in packed columns
  - Targeted carbonation in porous media flow
  - Targeted Carbonation of fractured wellbore-zone materials
- Imaging quantification of carbonation in pore networks and fractures
  - 3D imaging of targeted carbonation in porous media
  - 3D Imaging of targeted carbonation in fractured wellbore-zone materials
- Modeling Targeted Carbonation
  - Multiphase fluid mixing and flow modeling
  - Pore network/fracture reactive transport modeling
  - Forward modeling of mitigated wellbore integrity

accomplishments to date

- Discovered secondary mineral phase precipitates in the pseudowollastonite/CO_2 system
- Actively working to characterize the properties of these precipitates
- Observed dramatic permeability reductions when these minerals form and there could be synergies with $CaCO_3$
- Are characterizing these permeability reductions based on xCT analysis of pore structure
- Synthesized coatings with a LCST of 40°C
- Developed 1D model of column dynamics to help understand the reaction kinetics and transport dynamics in our system
- Built an experimental test-rig to evaluate the performance of these cements in fractures

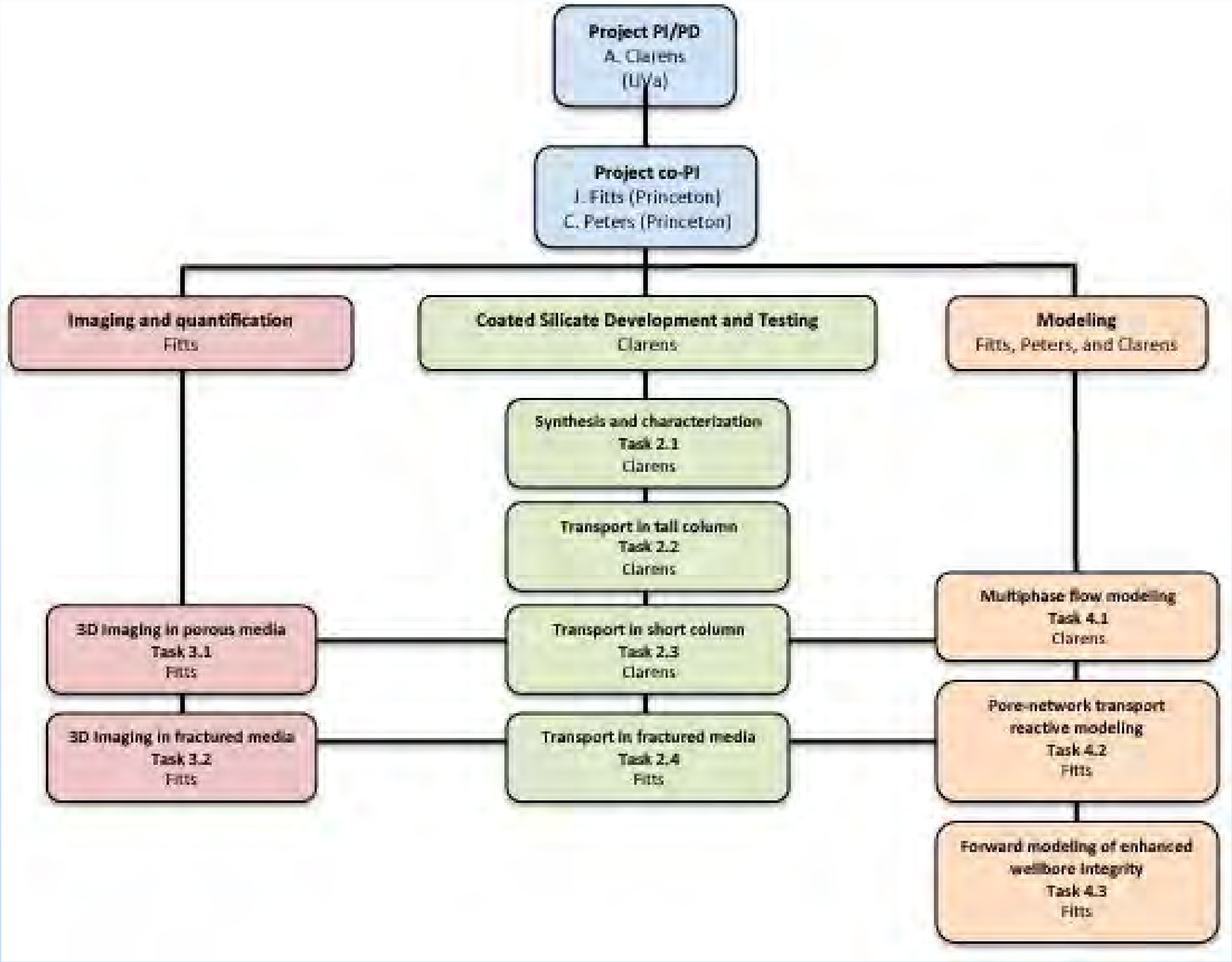
synergy opportunities

- w/ other PIs in this program:
  - Experience with nanoparticles use in fractures and porous media
    - Functionalization
    - Transport
    - Modeling
- w/ other PIs in Basalt storage area:
  - Reaction of carbonates in high P_{CO2} environments where the interplay between dissolution and precipitation needs to be controlled

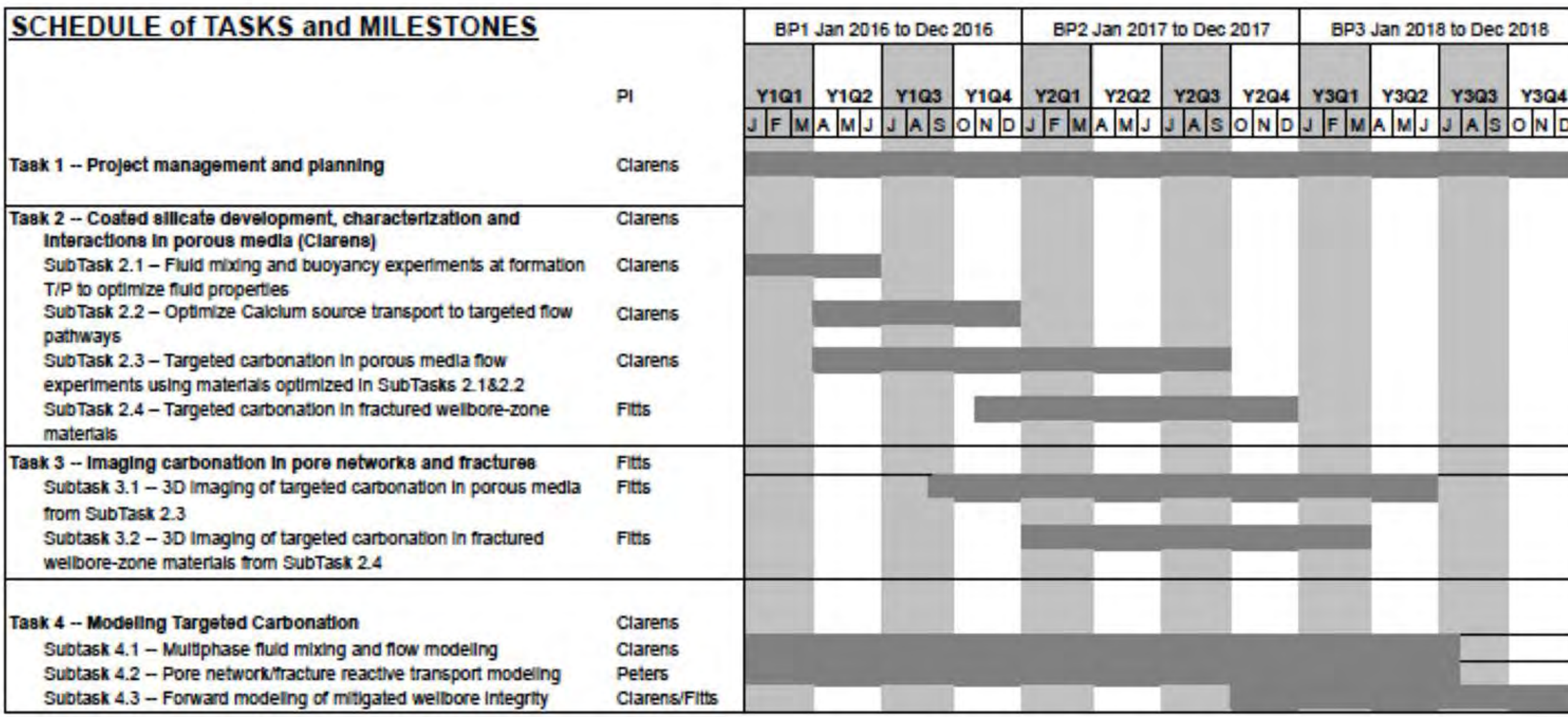
project summary

- Mineral silicates can be used to cement porous media and reduce its permeability when delivered as nanoparticles and exposed to a high P_{CO2} environment
- The unanticipated formation of silicate hydrates, driven by the presence of low partial pressures of CO_2, could be an important step to producing stable cements
- Significant drops in permeability have been observed and these precipitates are very resistant to re-dissolution in the presence of CO_2.
- Temperature sensitive coatings appear to be able to help us selectively deploy these materials at the desired depths

Organization Chart



Gantt Chart


SCHEDULE of TASKS and MILESTONES
PI
BP1 Jan 2016 to Dec 2016
BP2 Jan 2017 to Dec 2017
BP3 Jan 2018 to Dec 2018
Y1Q1 Y1Q2 Y1Q3 Y1Q4 Y2Q1 Y2Q2 Y2Q3 Y2Q4 Y3Q1 Y3Q2 Y3Q3 Y3Q4
J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D
Task 1 -- Project management and planning
Clarens
Task 2 -- Coated silicate development, characterization and interactions in porous media (Clarens)
Clarens
SubTask 2.1 – Fluid mixing and buoyancy experiments at formation T/P to optimize fluid properties
Clarens
SubTask 2.2 – Optimize Calcium source transport to targeted flow pathways
Clarens
SubTask 2.3 – Targeted carbonation in porous media flow experiments using materials optimized in SubTasks 2.1&2.2
Clarens
SubTask 2.4 – Targeted carbonation in fractured wellbore-zone materials
Fitts
Task 3 -- Imaging carbonation in pore networks and fractures
Fitts
Subtask 3.1 -- 3D imaging of targeted carbonation in porous media from SubTask 2.3
Fitts
Subtask 3.2 -- 3D imaging of targeted carbonation in fractured wellbore-zone materials from SubTask 2.4
Fitts
Task 4 -- Modeling Targeted Carbonation
Clarens
Subtask 4.1 -- Multiphase fluid mixing and flow modeling
Clarens
Subtask 4.2 -- Pore network/fracture reactive transport modeling
Peters
Subtask 4.3 -- Forward modeling of mitigated wellbore integrity
Clarens/Fitts

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