Targeted Mineral Carbonation to Enhance Wellbore Integrity

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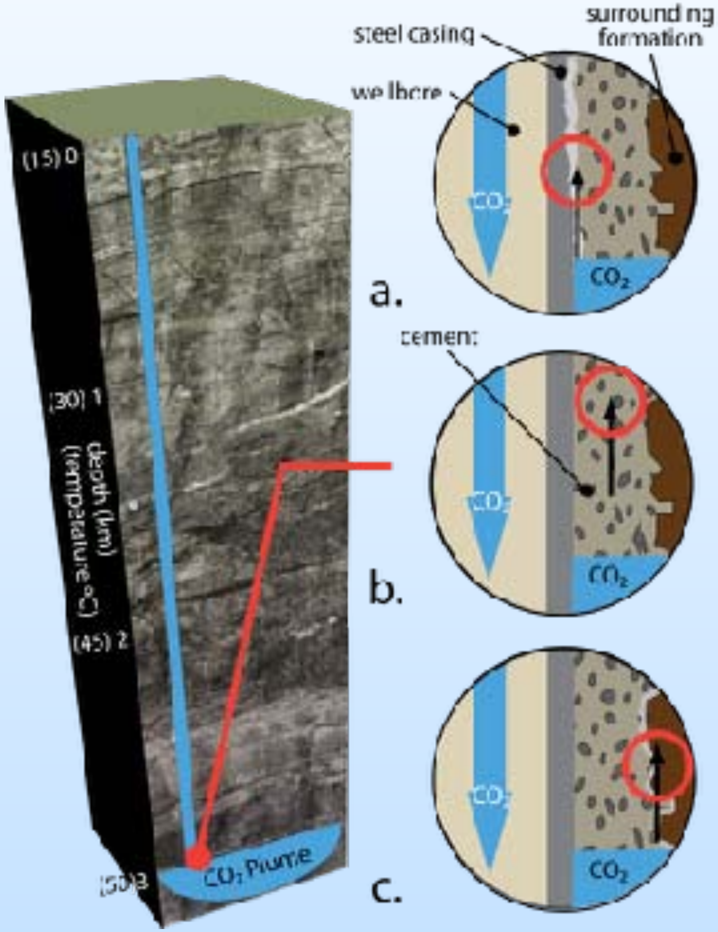
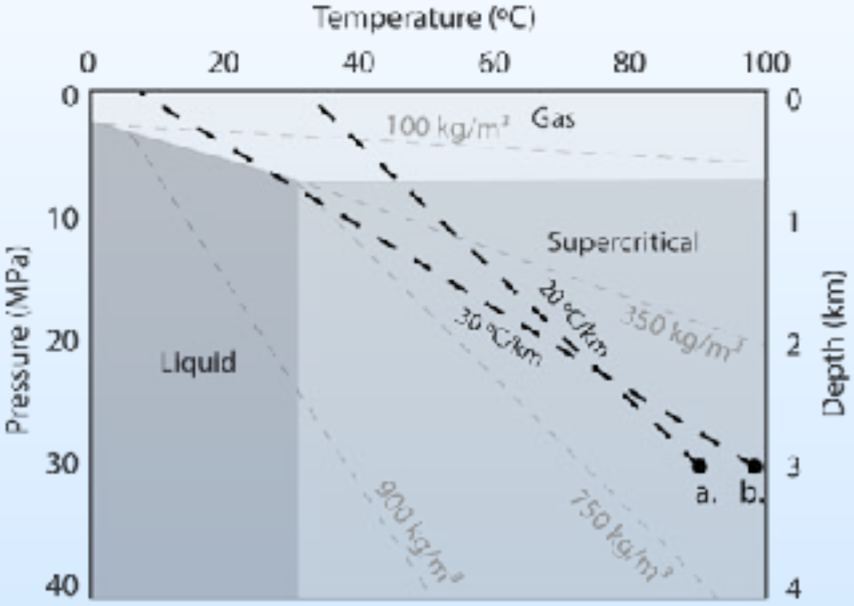
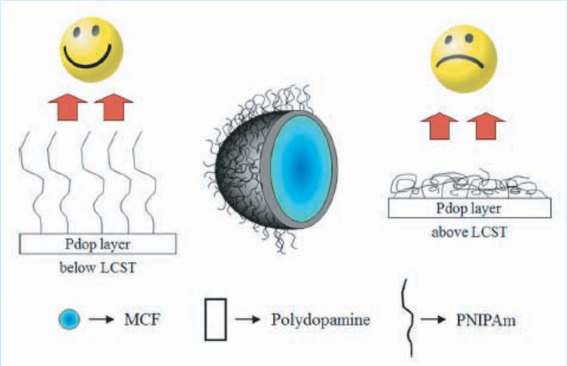
U.S. Department of Energy
National Energy Technology Laboratory
Mastering the Subsurface Through Technology, Innovation and Collaboration:
Carbon Storage and Oil and Natural Gas Technologies Review Meeting
August 2, 2017

the concept

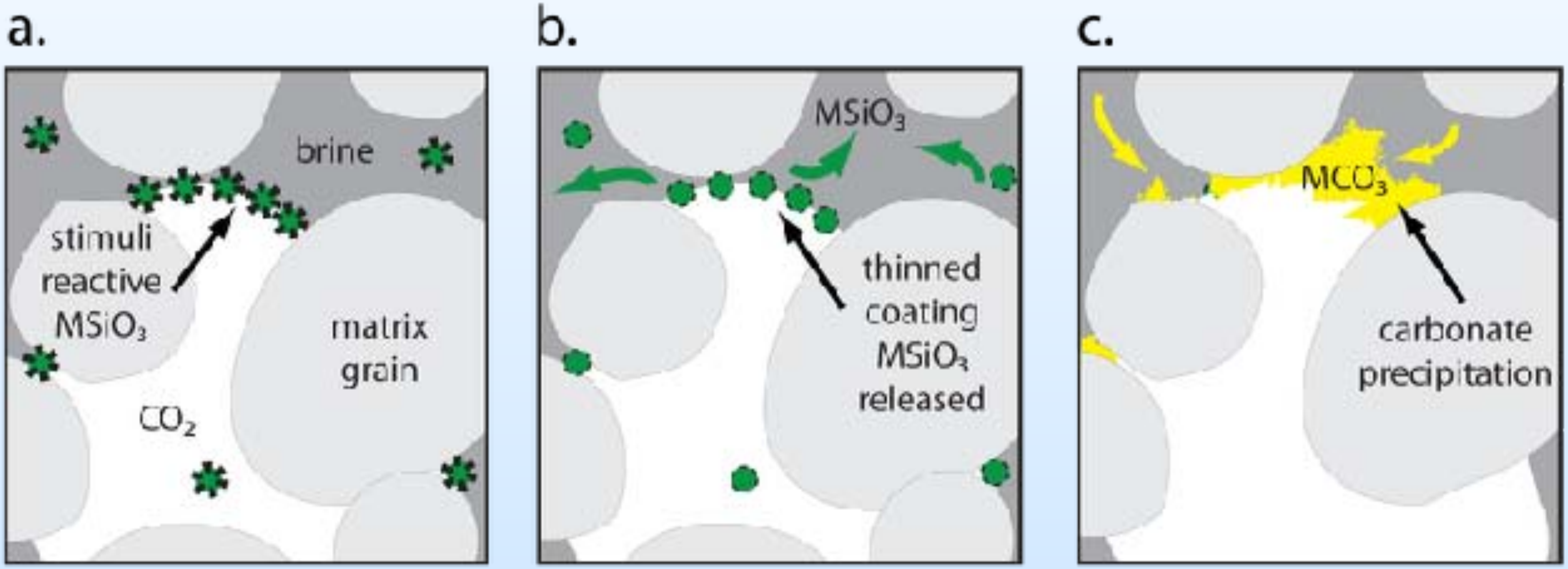






Ma et al 2013

underlying principle

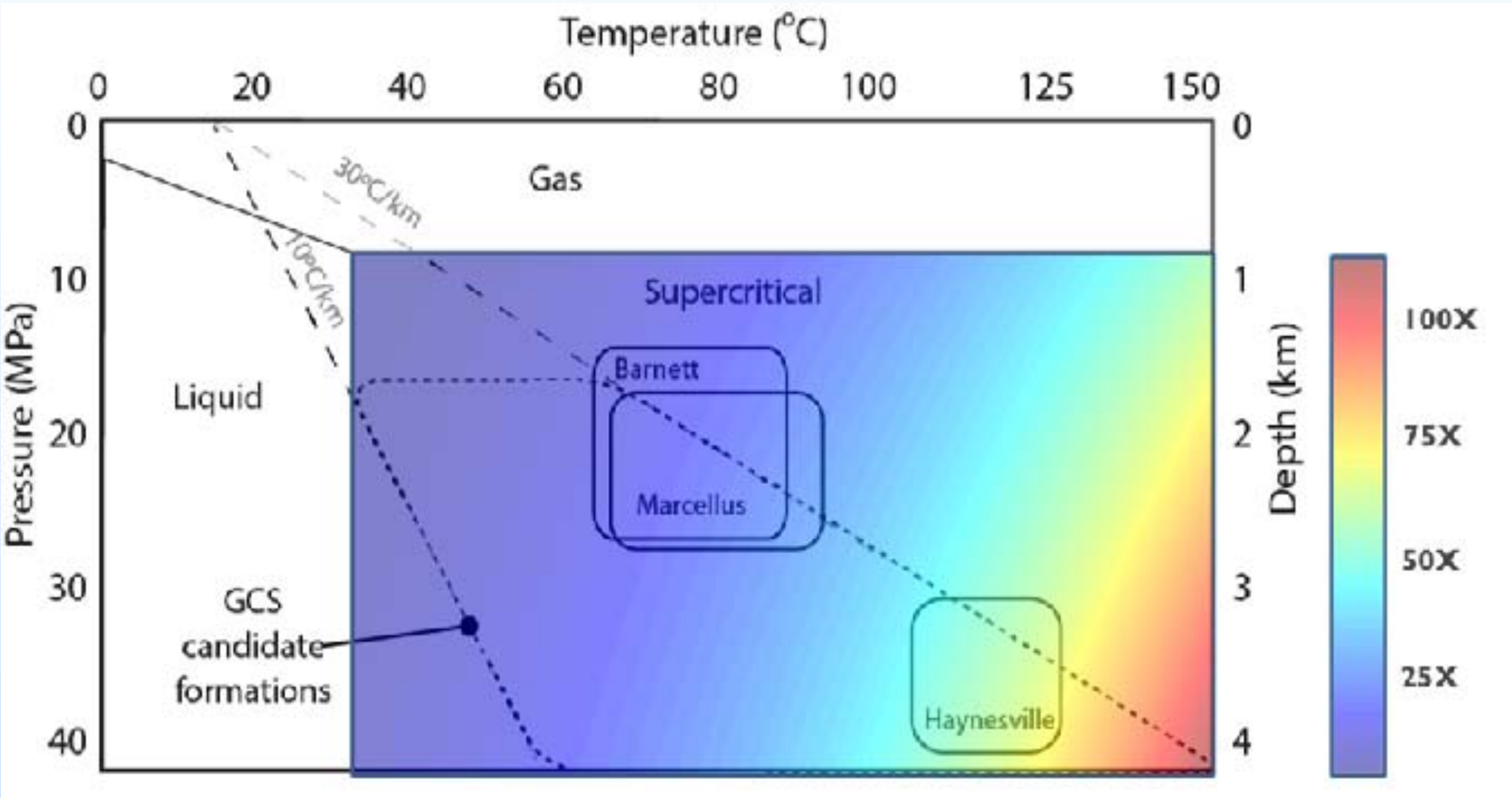


$T > T_C$
$MSiO_3$ contained
Buoyancy flow

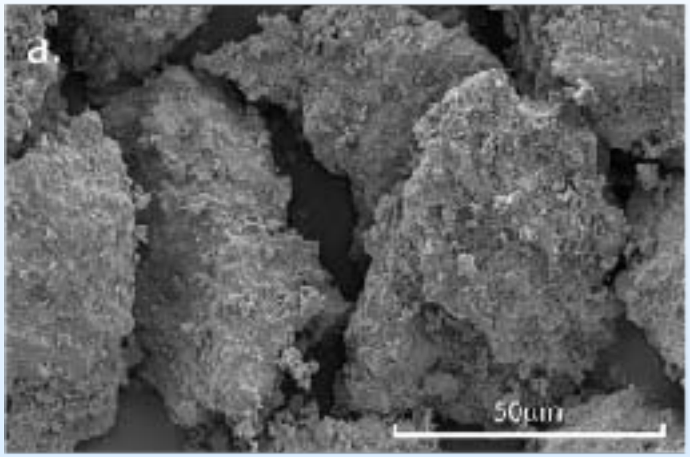
$T < T_C$
$MSiO_3$ released
Buoyancy flow

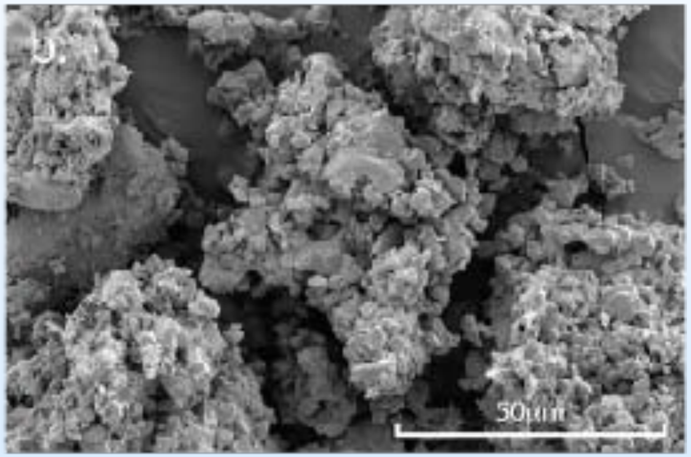
$T < T_C$
MCO_3 precipitated
Pores blocked, no flow

reaction kinetics vs. depth

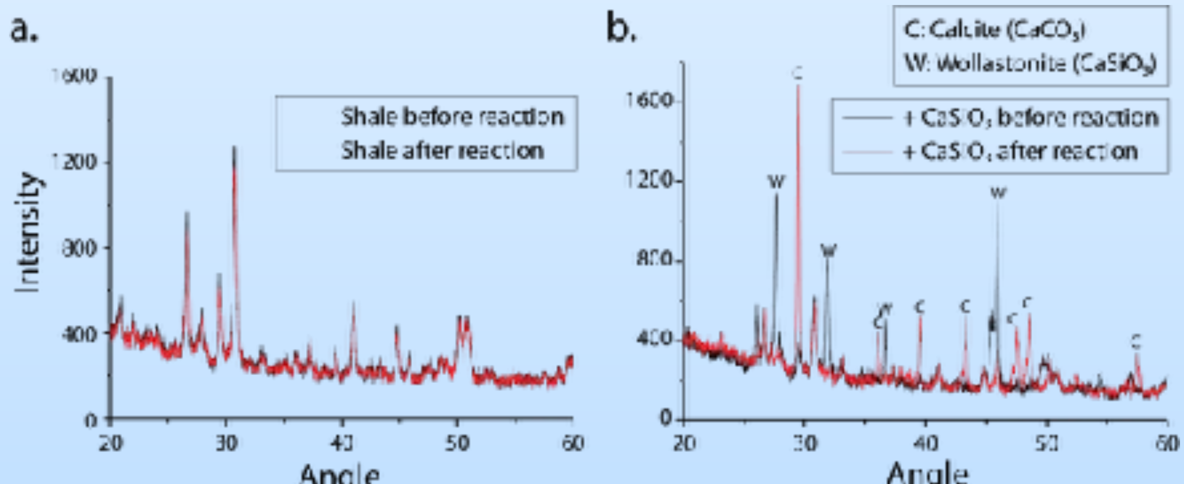


early results





shale grains   shale grains + CO_2 + $CaSiO_3$



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

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

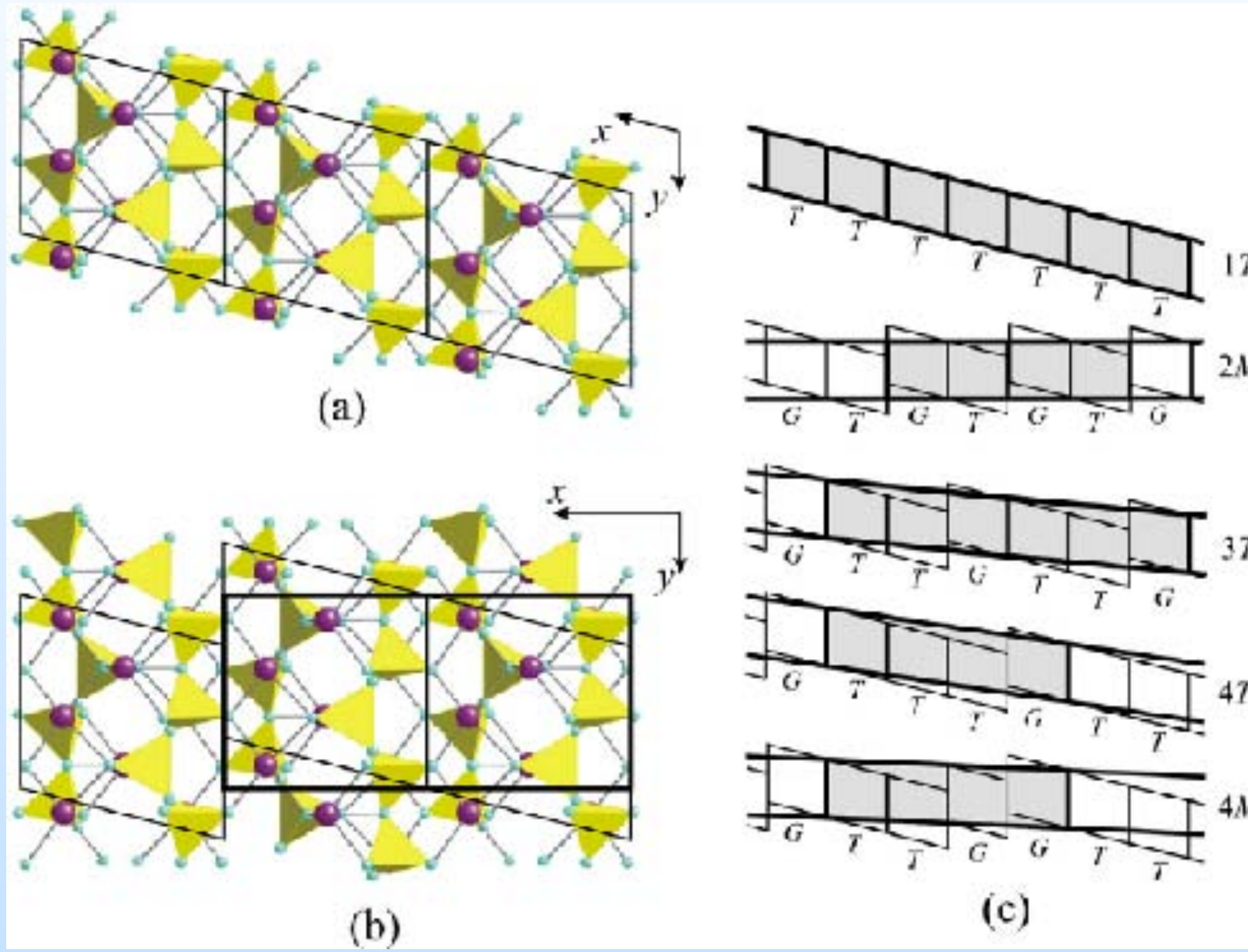
nanoparticle core

mineral	reaction	E_a (kJ/mol)
basaltic glass	$MgSiO_3 + CO_2 = MgCO_3 + SiO_2$	80.0
olivine	$MgSiO_4 + 2CO_2 = 2MgCO_3 + 2SiO_2$	76.2
serpentine	$Mg_3Si_2O_5(OH)_4 + 3CO_2 = 3MgCO_3 + 2SiO_2 + 2H_2O$	70.1
albite	$2NaAlSi_2O_8 + CO_2 = Na_2CO_3 + 6SiO_2 + Al_2O_3$	65.0
wollastonite	$CaSiO_3 + CO_2 = CaCO_3 + SiO_2$	54.7
talc	$Mg_3Si_4O_{10}(OH)_2 + 3CO_2 = 3MgCO_3 + 4SiO_2 + H_2O$	51.4
anorthite	$CaAl_2Si_2O_8 + CO_2 = CaCO_3 + 2SiO_2 + Al_2O_3$	48.4

pseudowollastonite v wollastonite

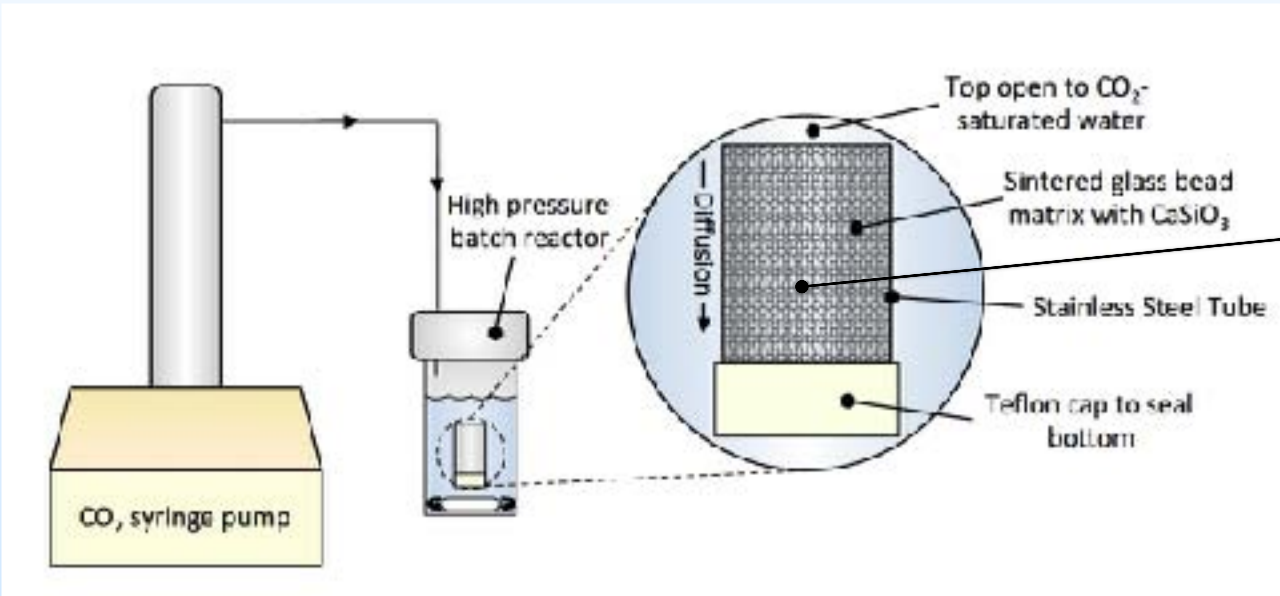
wollastonite

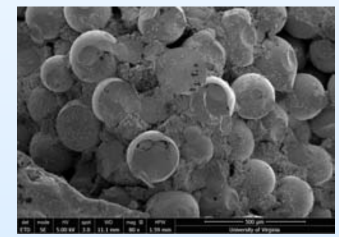
pseudo
wollastonite

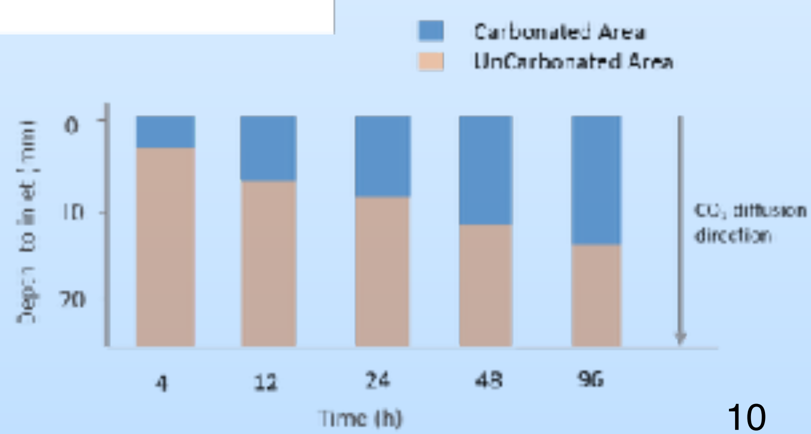


Seryotkin et al. Lithos 134 (2012): 75-90.

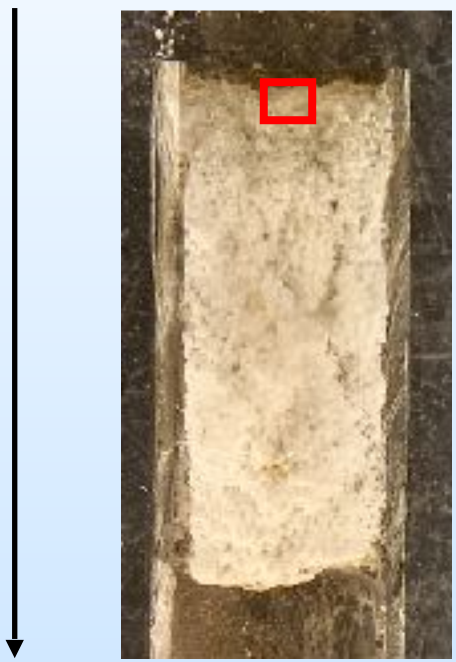
diffusion limited results - kinetics and transport

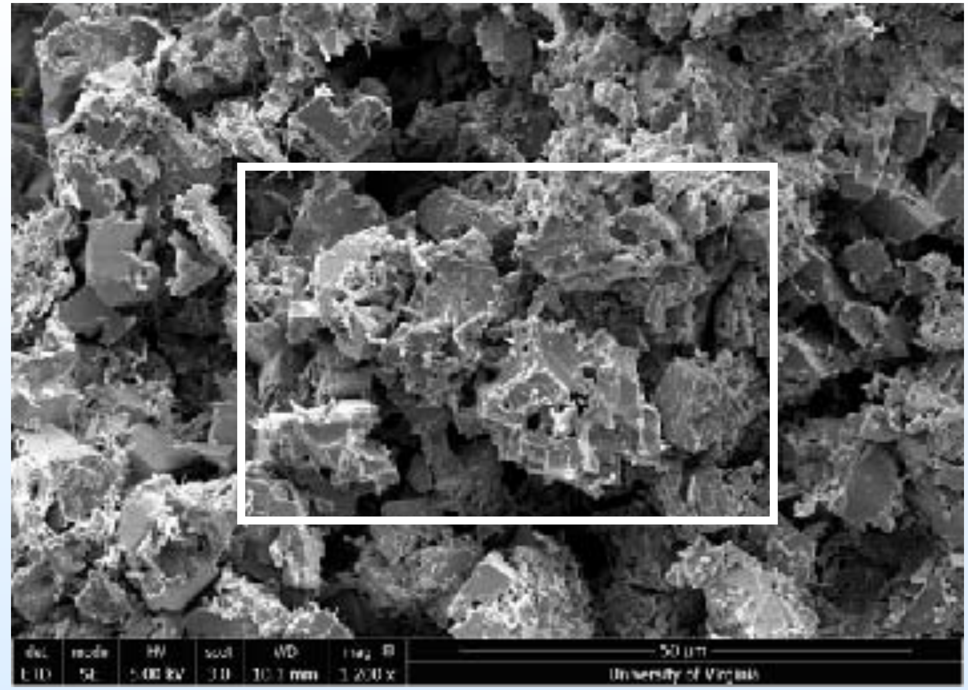


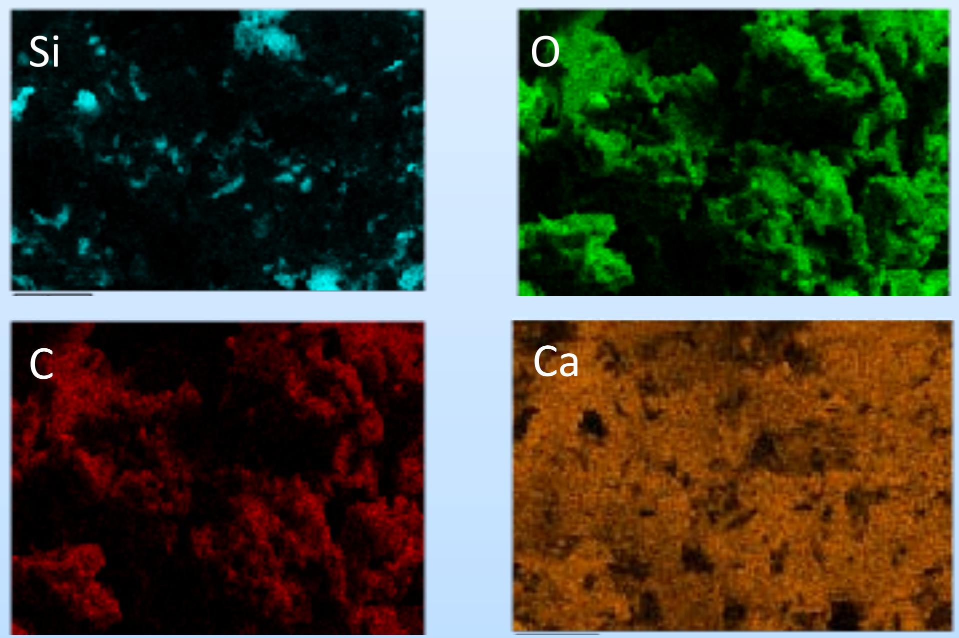




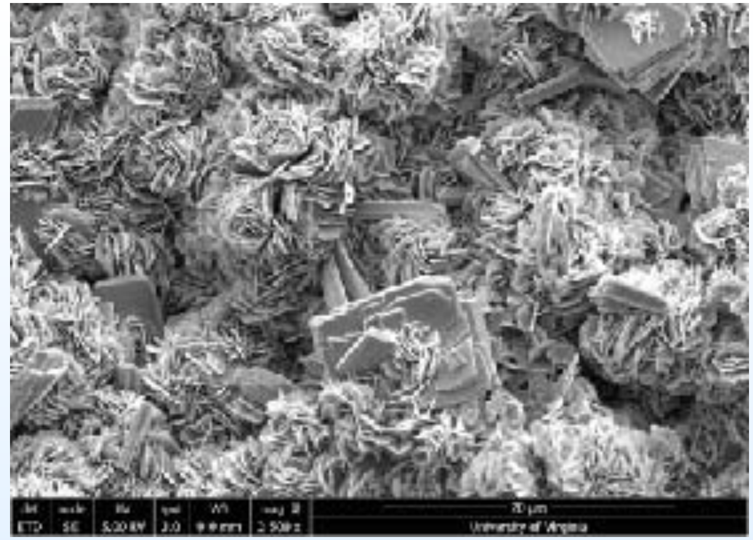
Diffusion

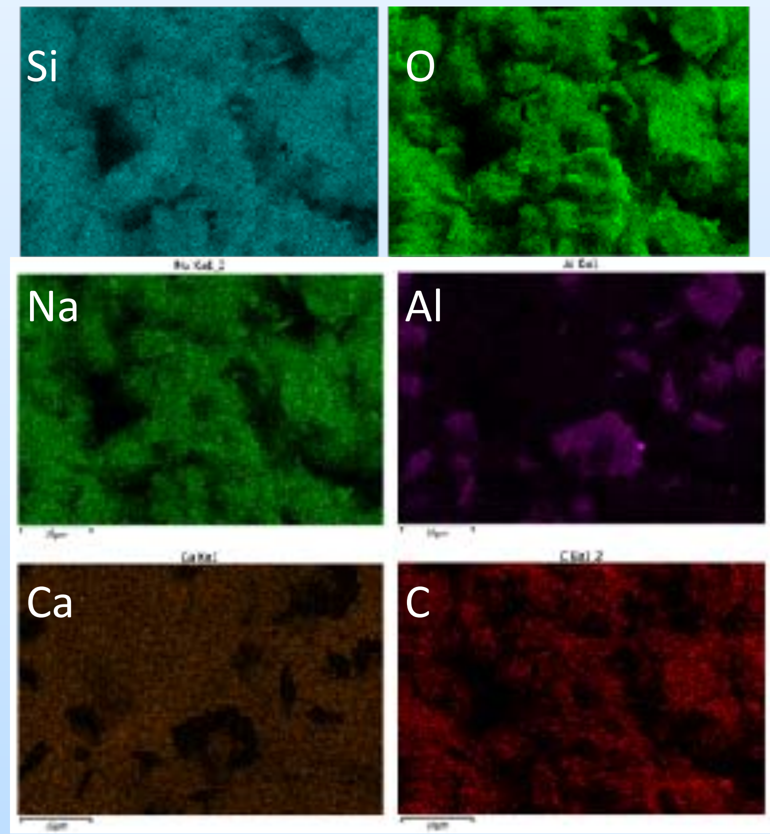




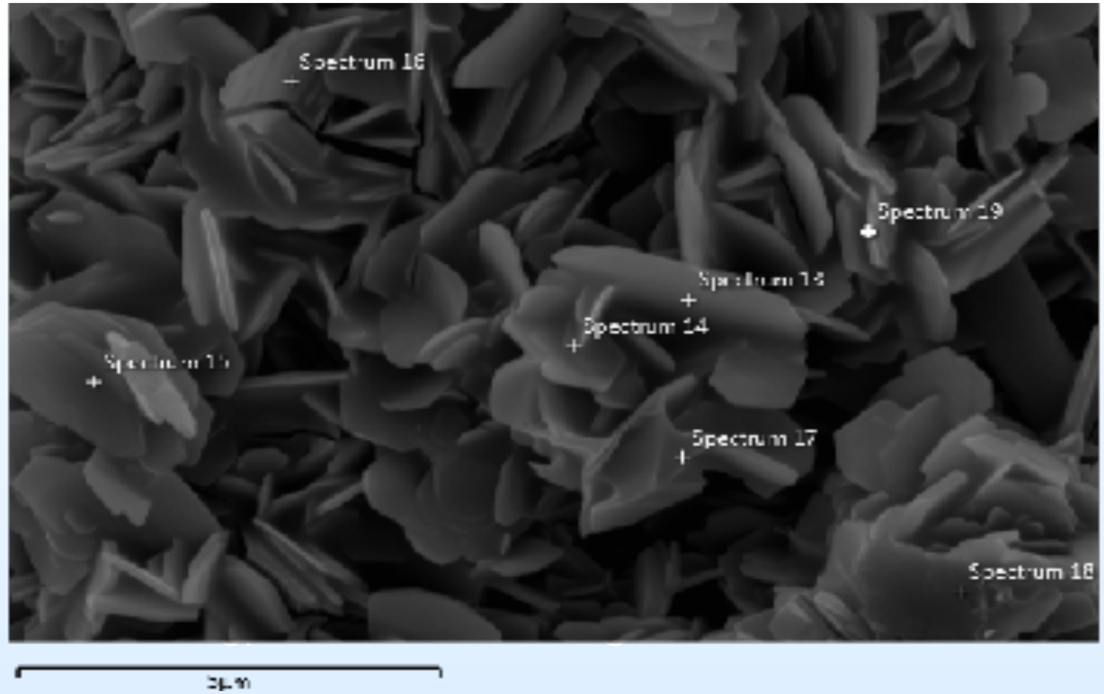


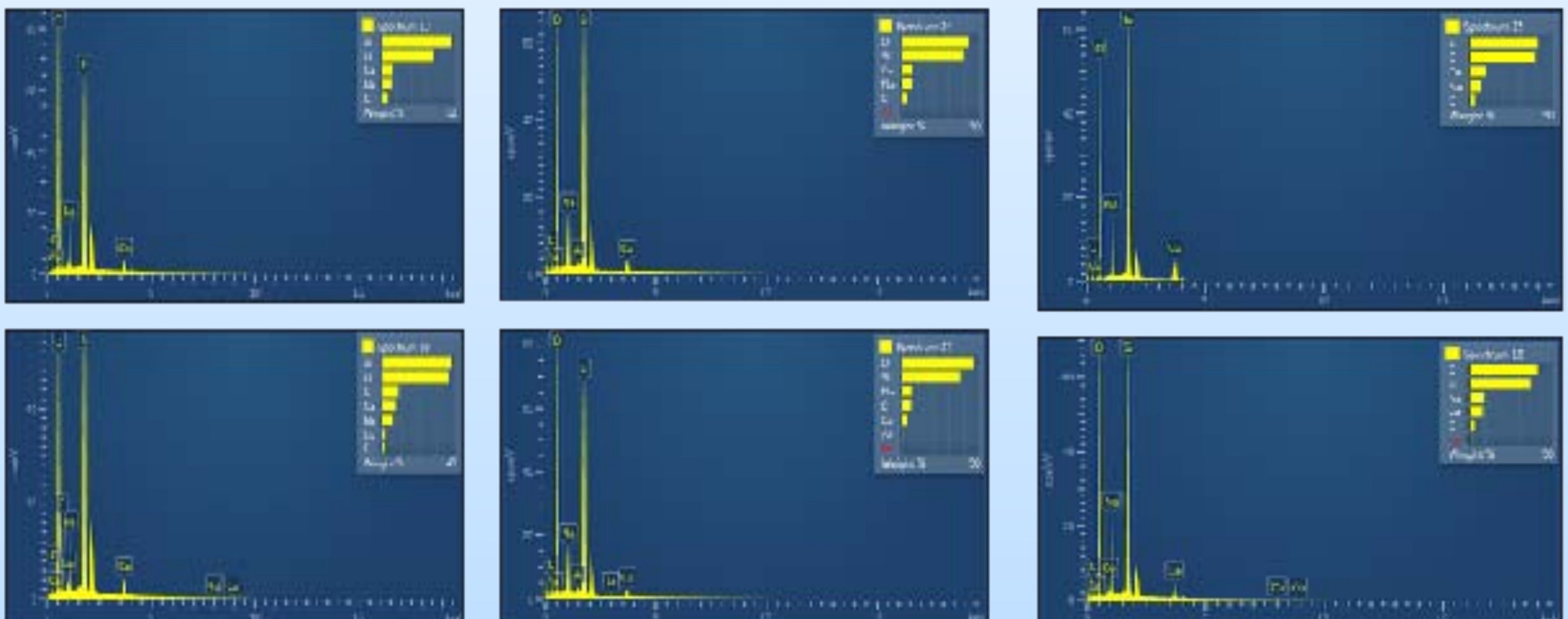
Diffusion





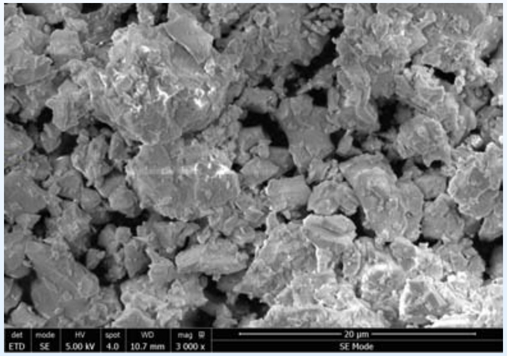
Diffusion

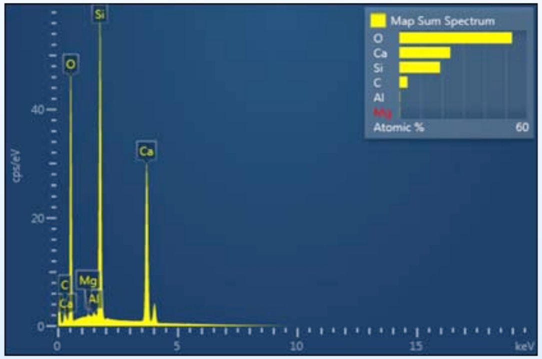

Spectrum 16
Spectrum 19
Spectrum 14
Spectrum 17
Spectrum 18



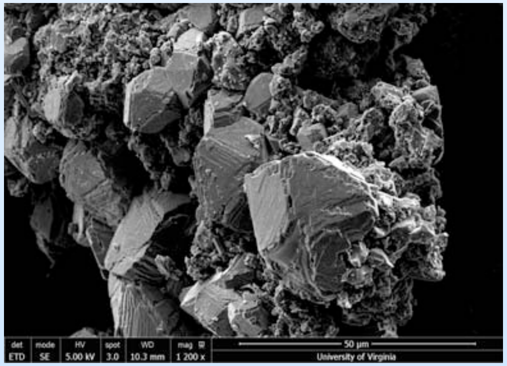
complex reaction pathway

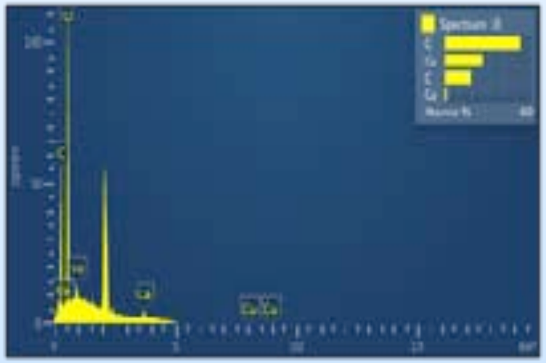
Unreacted Pseudowollastonite



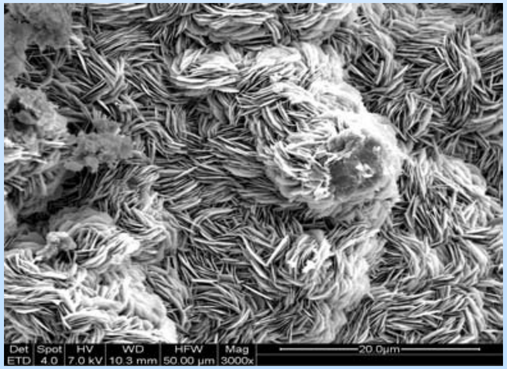


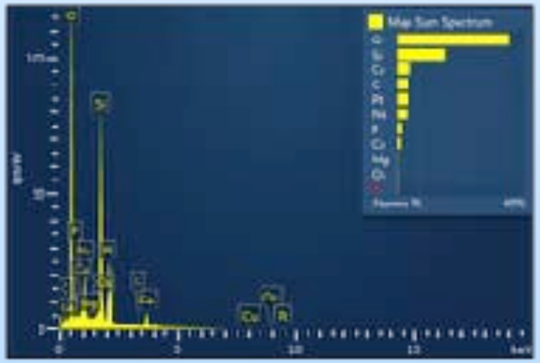
Calcium Carbonate



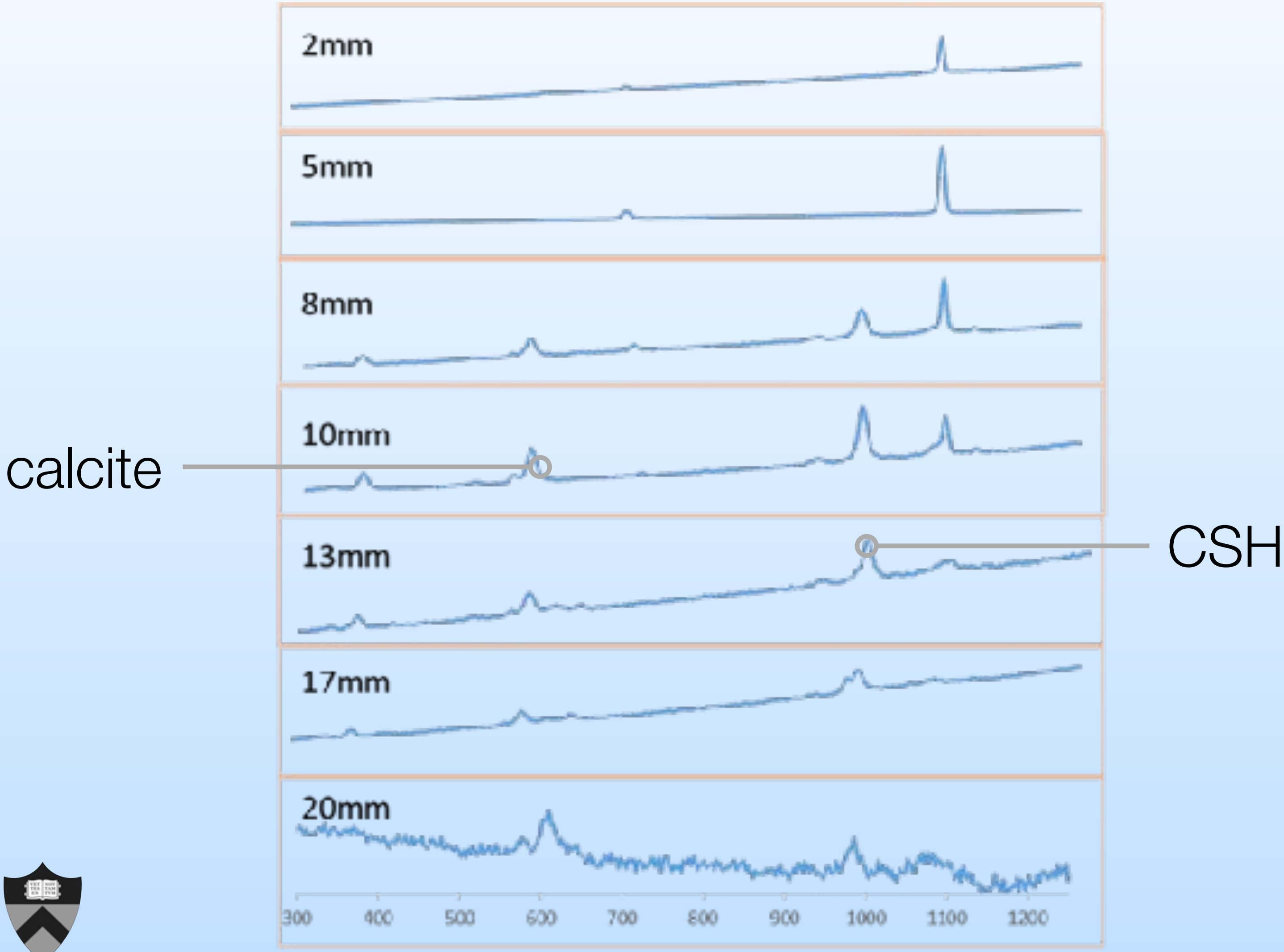


O-Si-Ca-C Phase

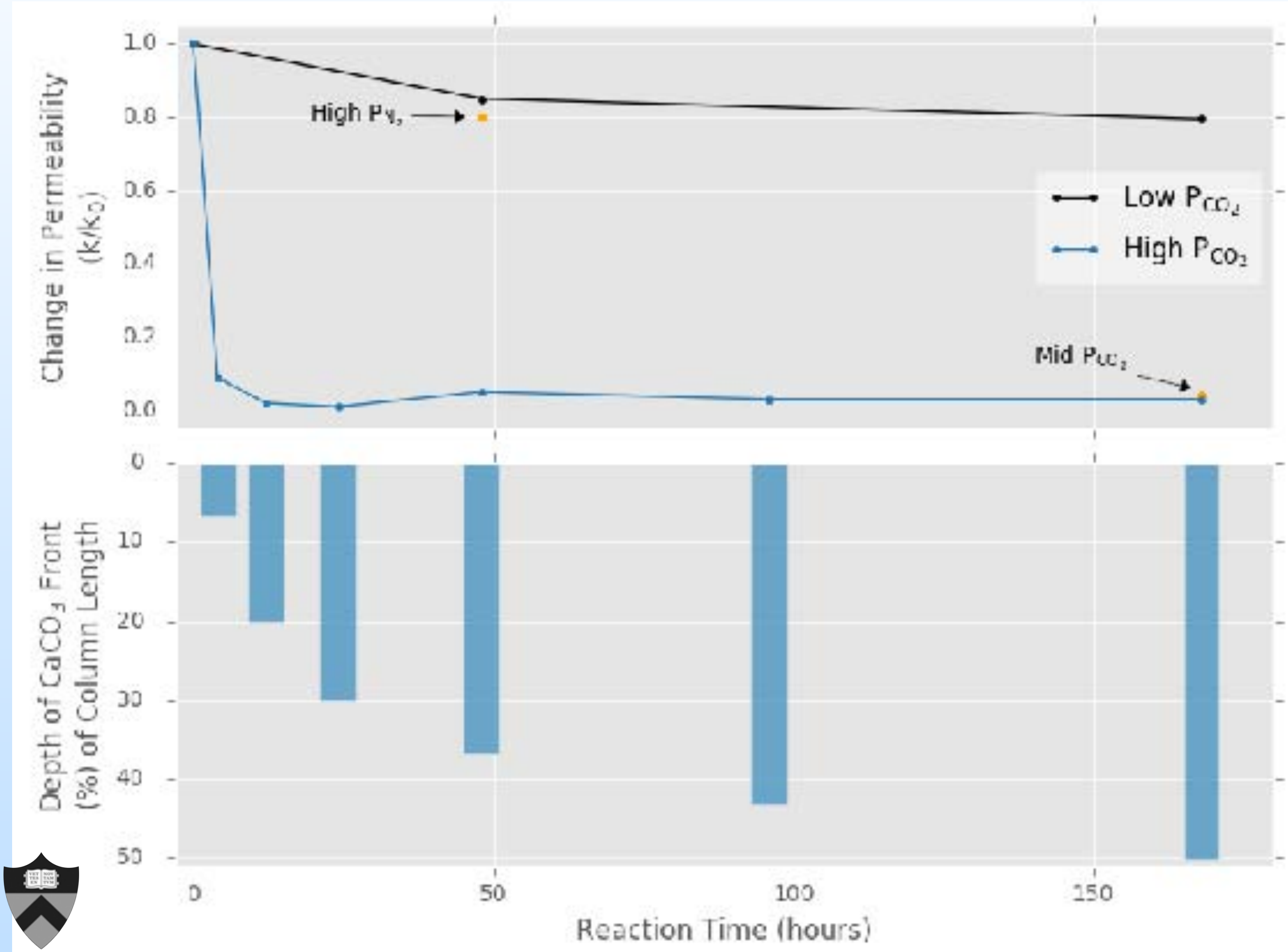




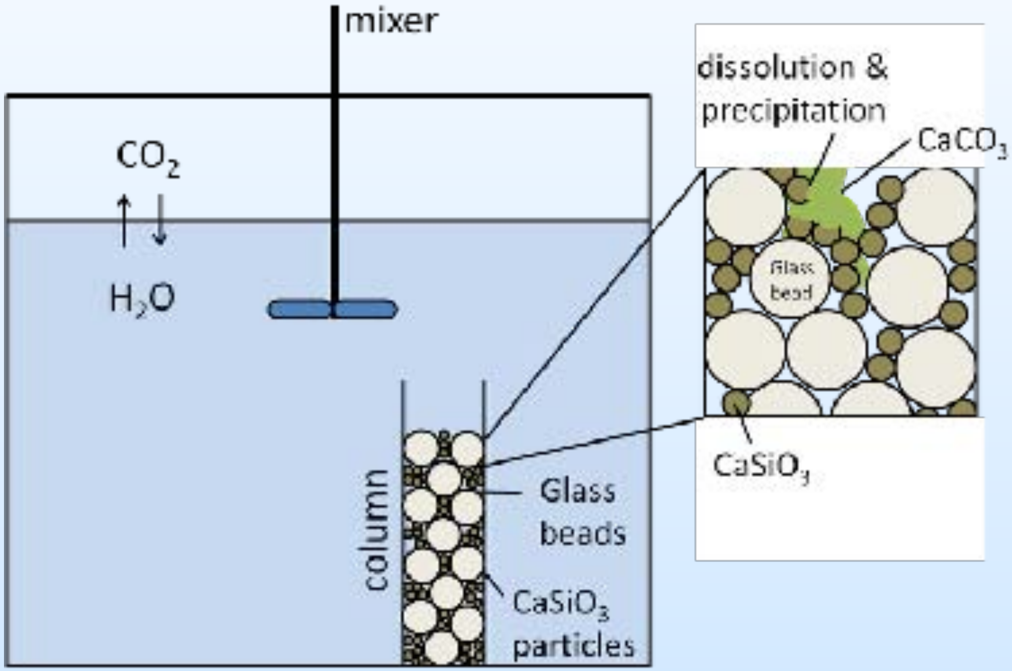
raman scans of column



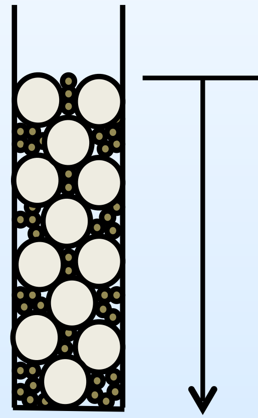
effects on permeability



1D geochemical modeling approach



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

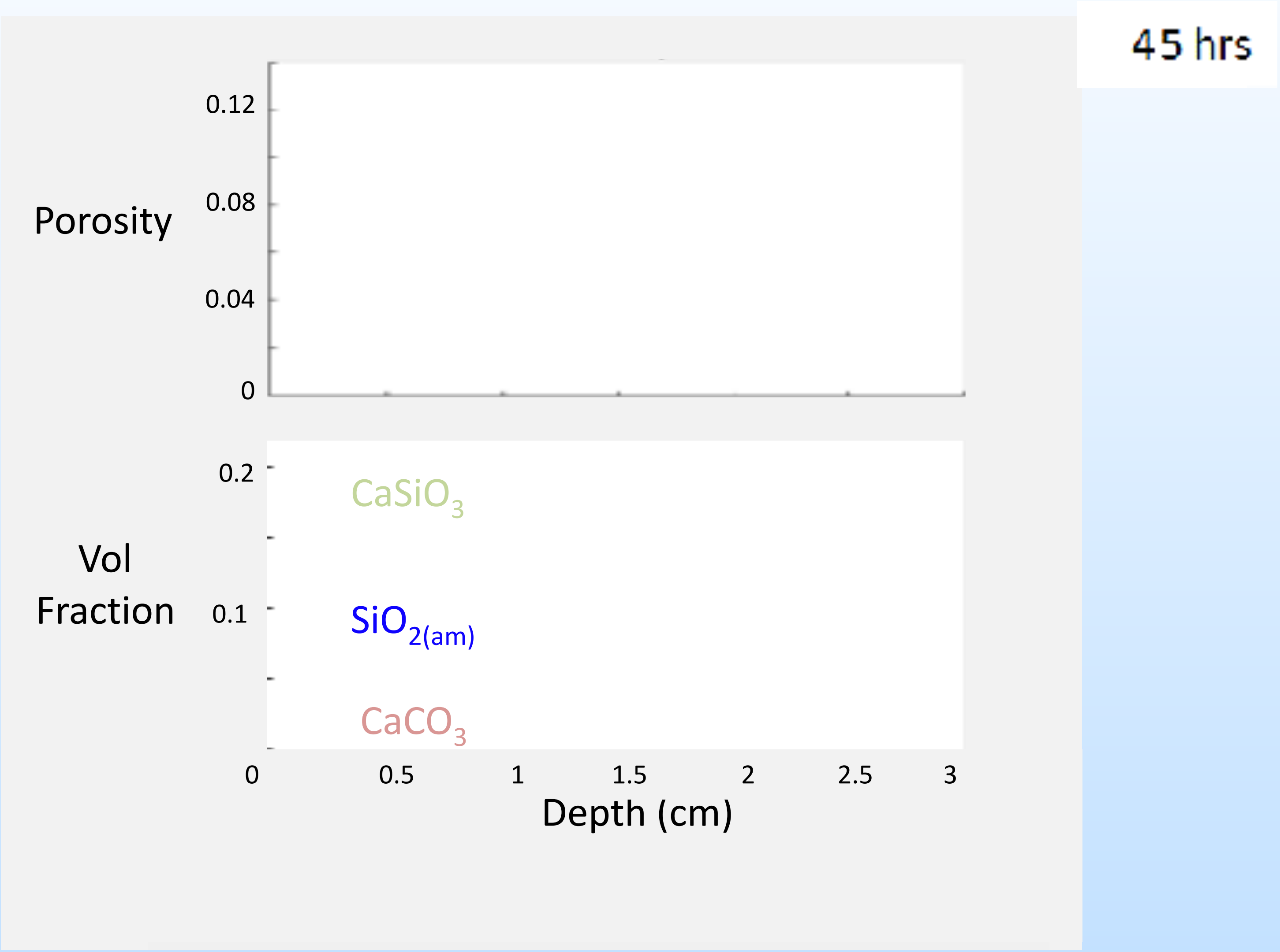
Reactions

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

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

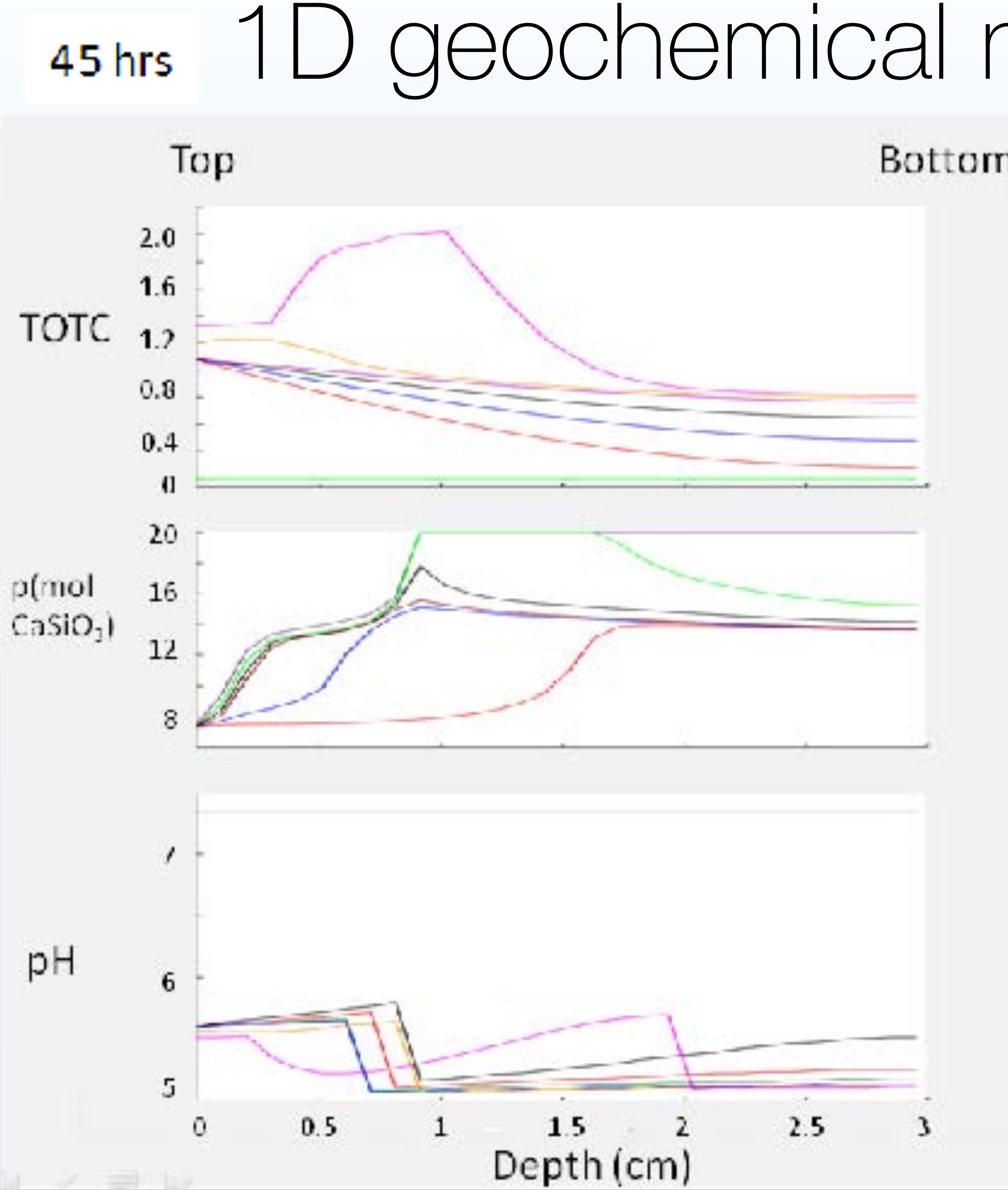
$$SiO_{2\,(aq)} \leftrightarrow SiO_{2\,(am)}$$

1D geochemical modeling results



$CaCO_3$ and $SiO_{2(am)}$ precipitation concentrate near the opening of the glass bead column, leading to significant porosity decrease by 45 hrs of reaction.

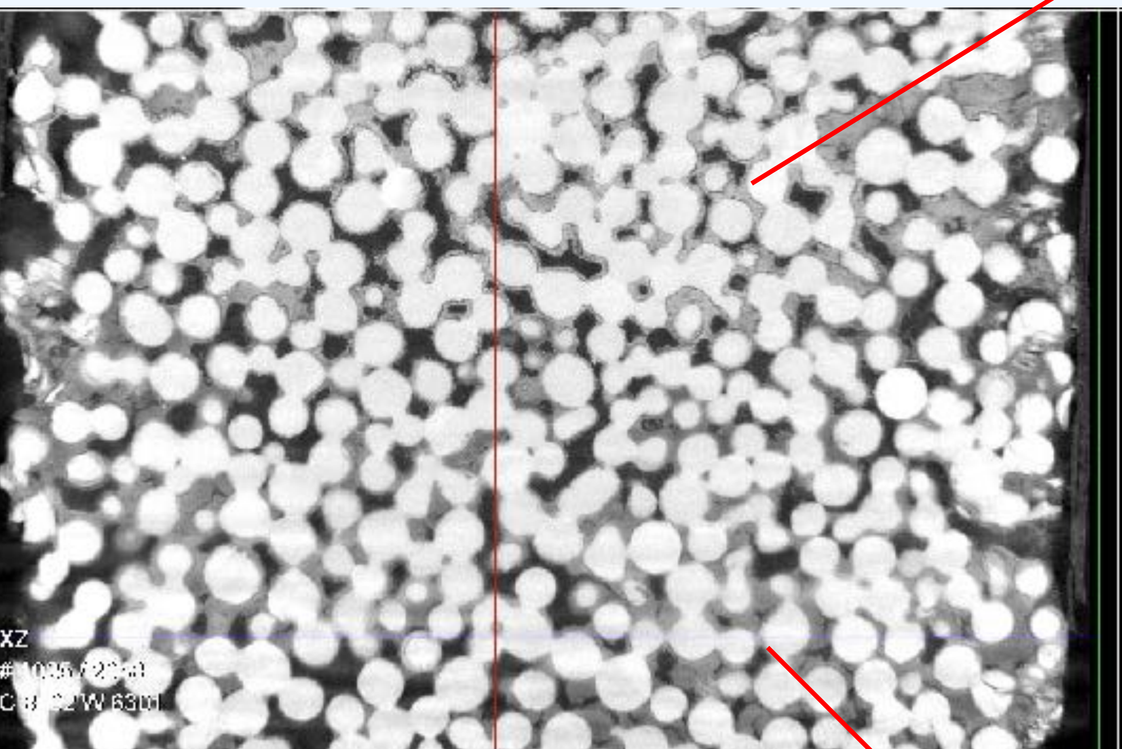
1D geochemical modeling results

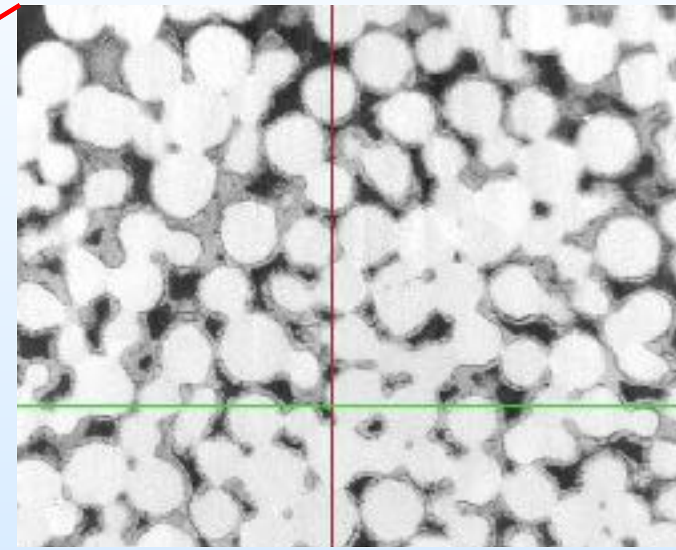


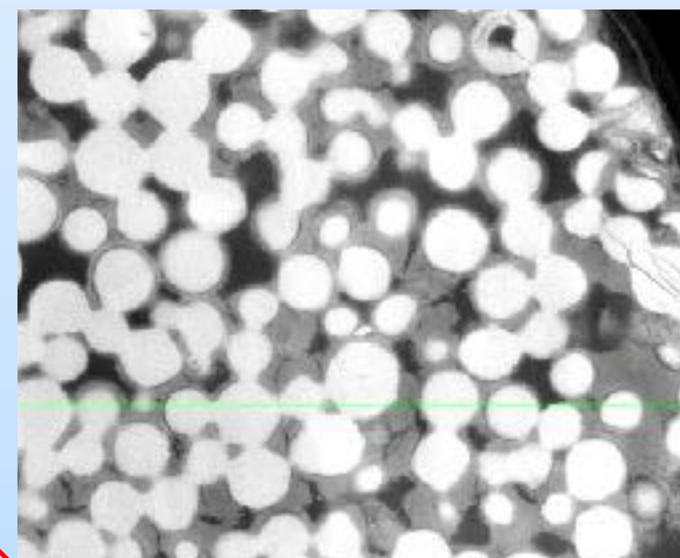
- CO_2 diffuses into the column, lowering pH.
- The pH increases as $CaSiO_3$ dissolves.
- The pH throughout the column is largely controlled by $CaSiO_3$ dissolution.
- Differences in pH and CO_2 at the top vs. bottom of the column may lead to the formation of unaccounted solids in the model.

xCT images of columns

Top



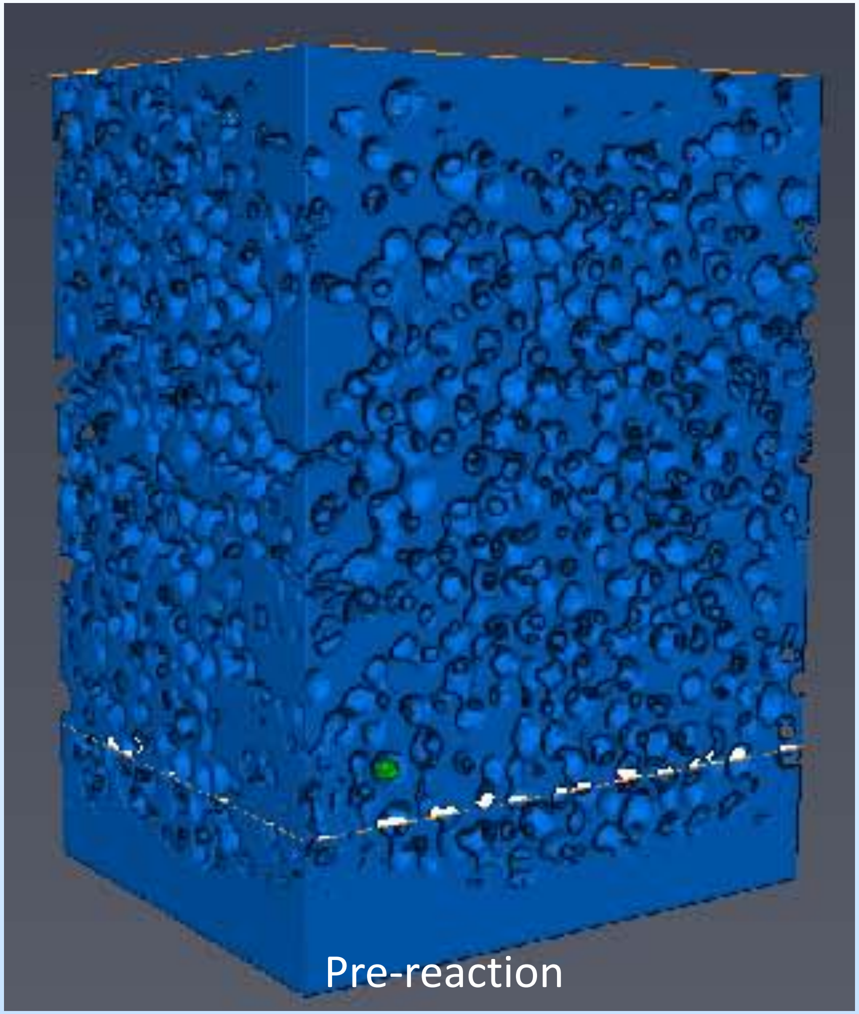


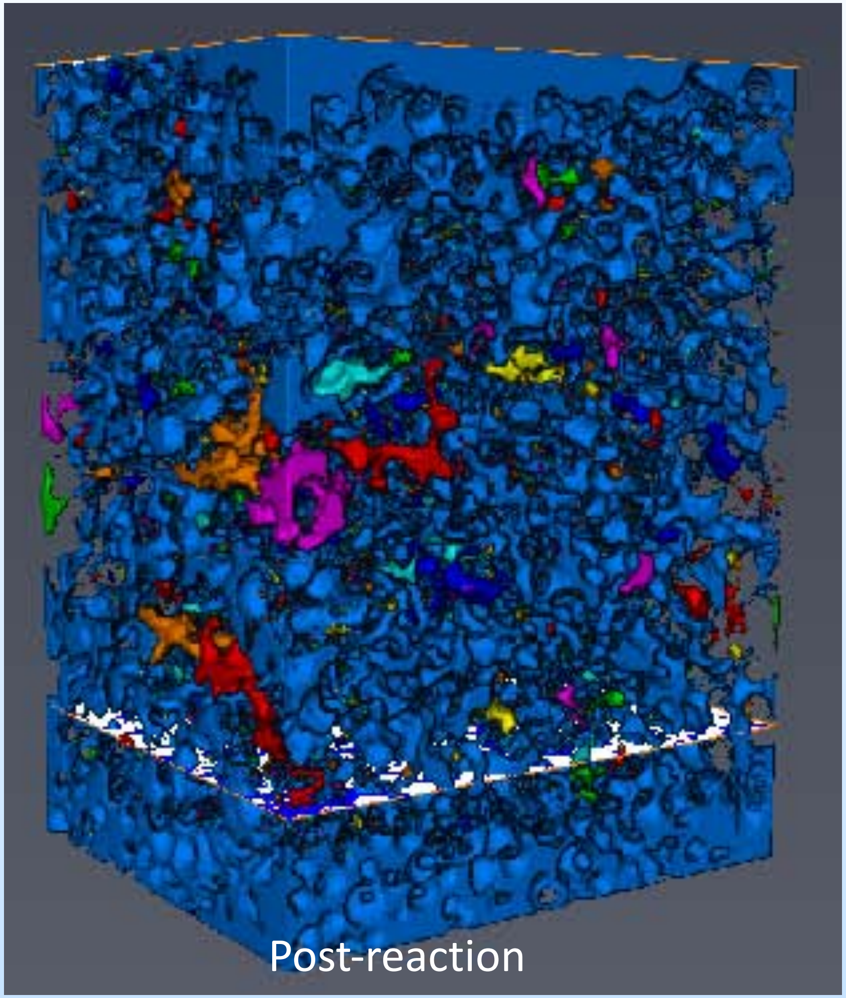


Bottom

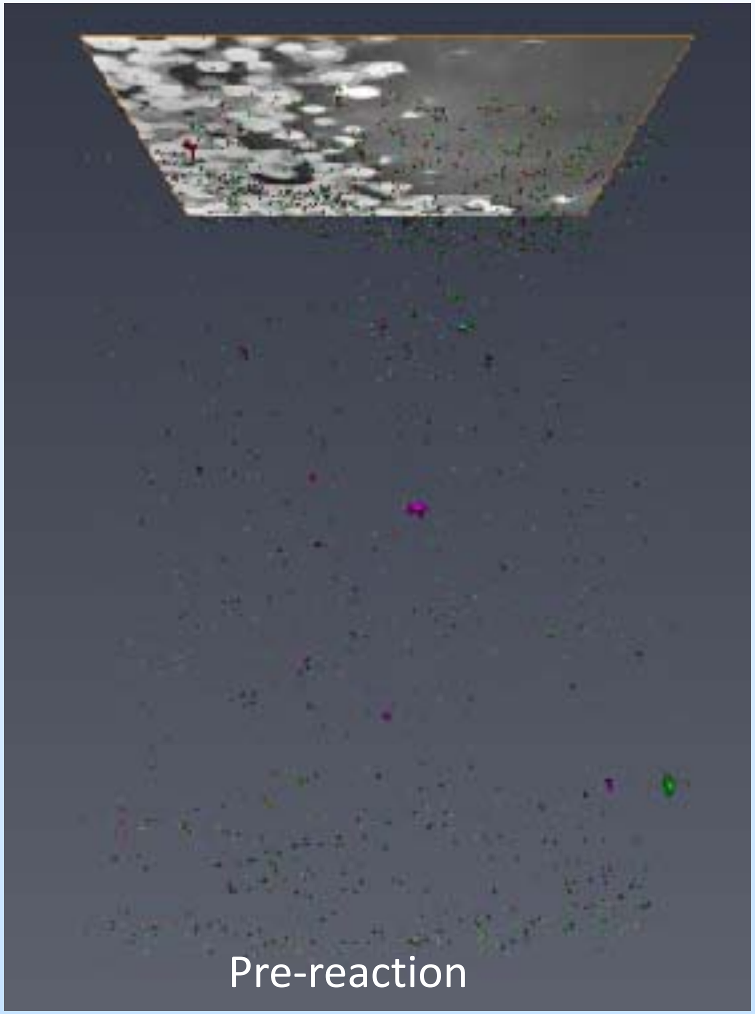
Differences exist in the density of the material filling the pore space at the top and bottom of the column.

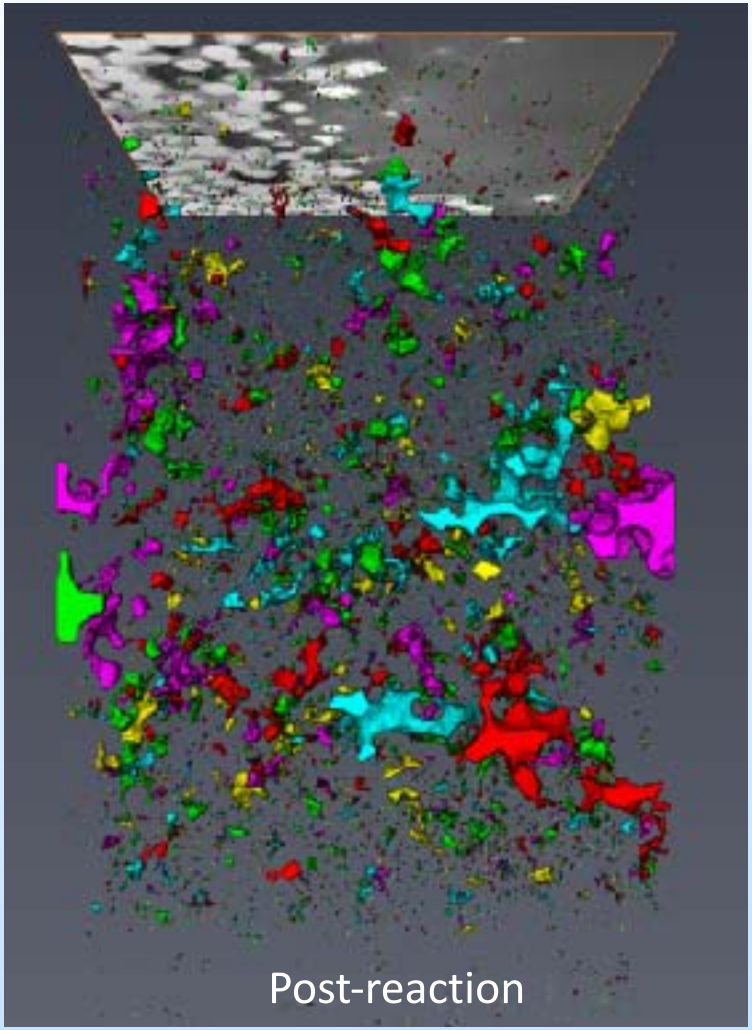
xCT images of columns



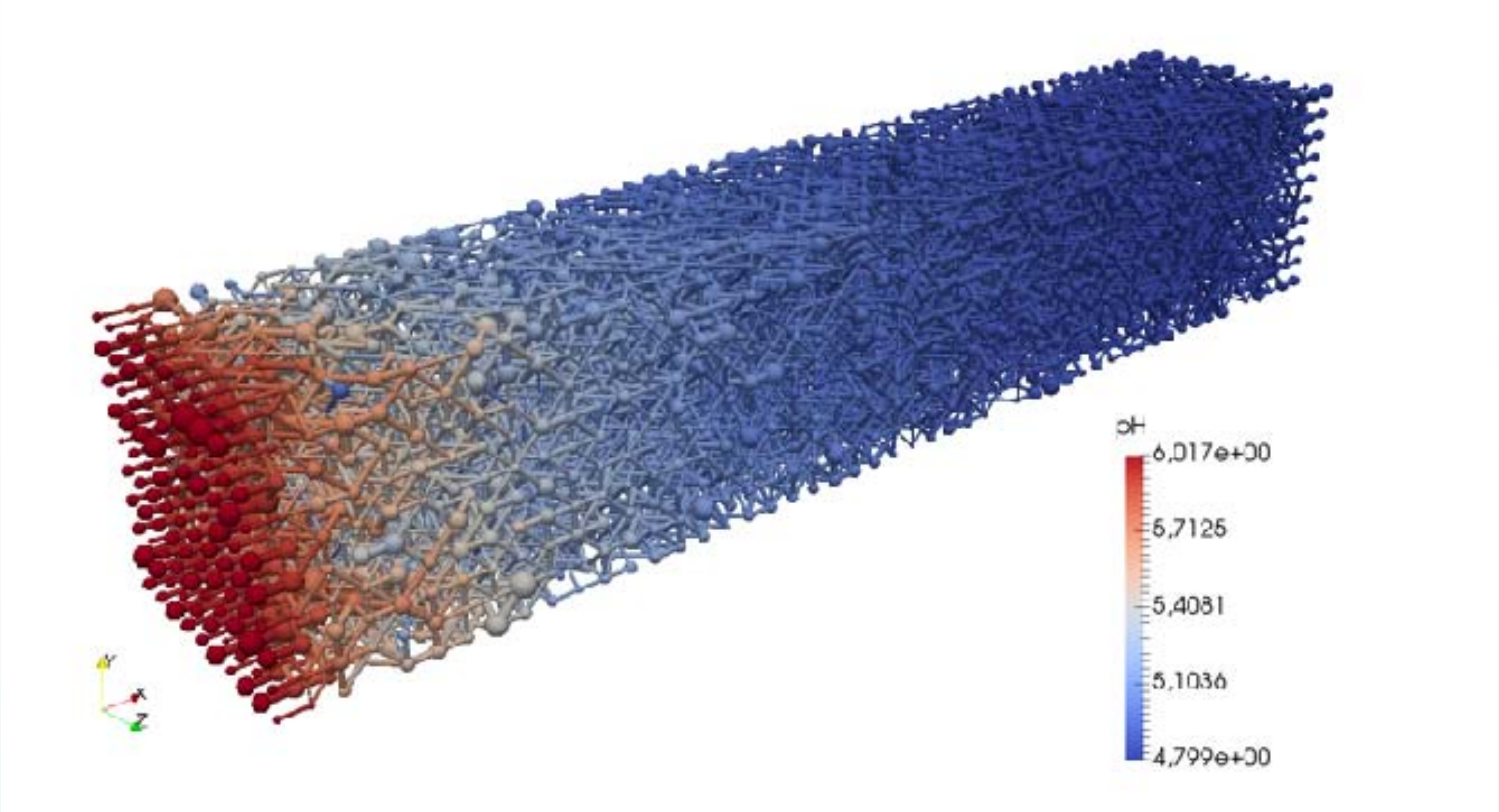


pore connectivity decrease



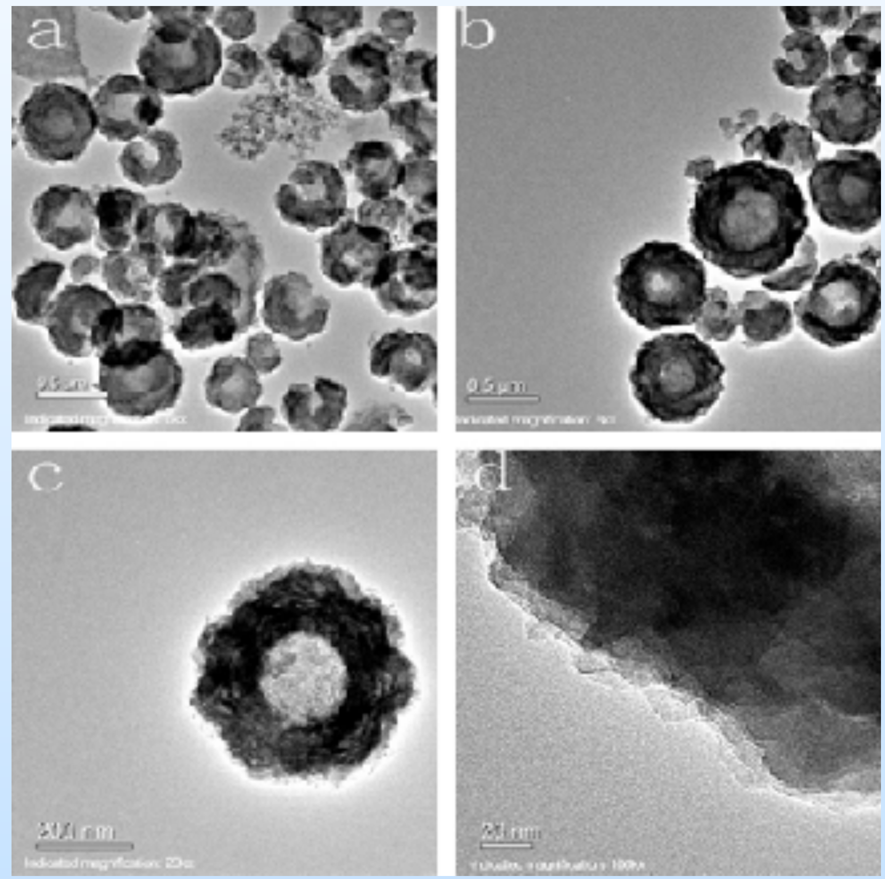


pore network modeling

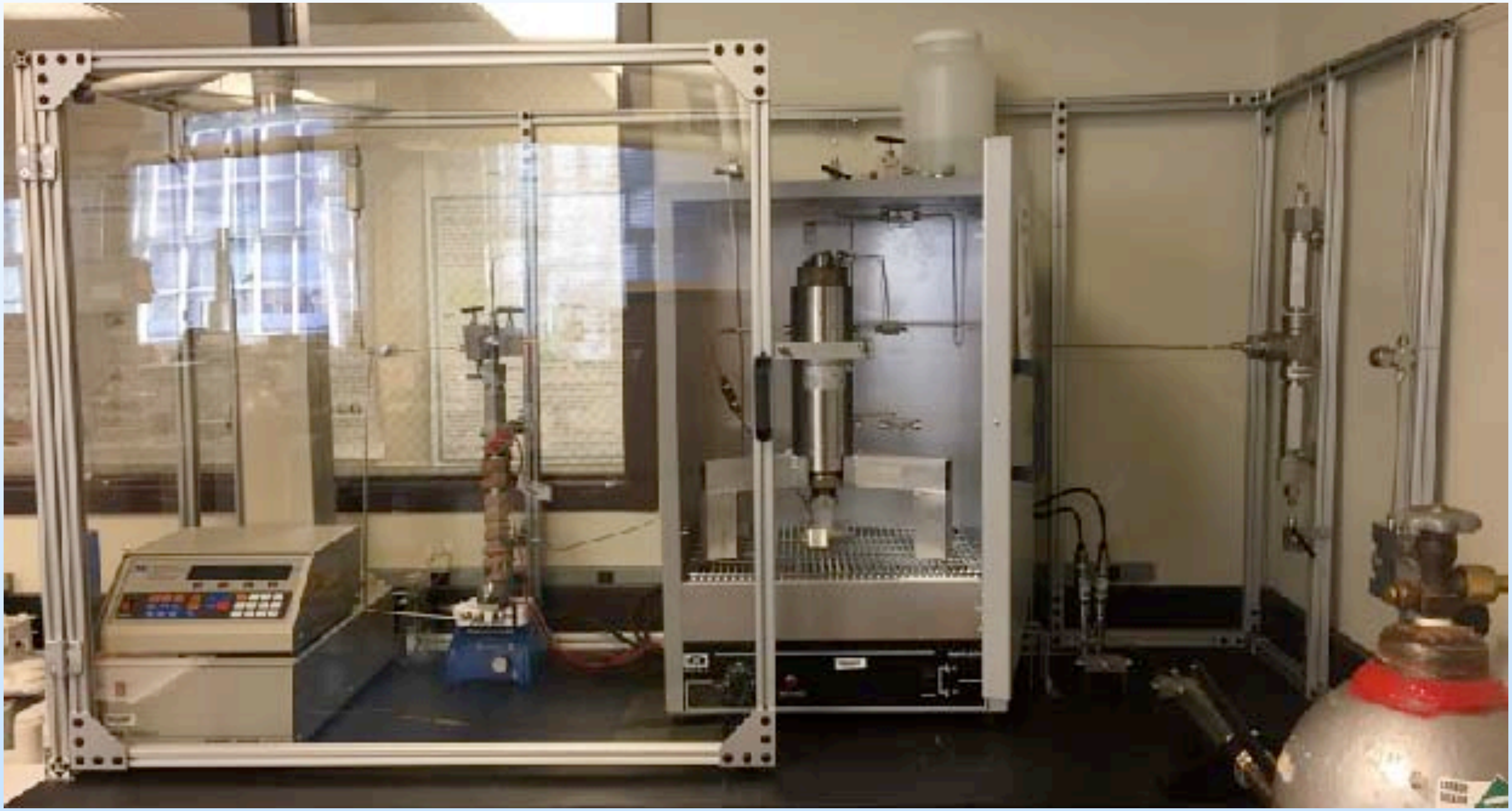


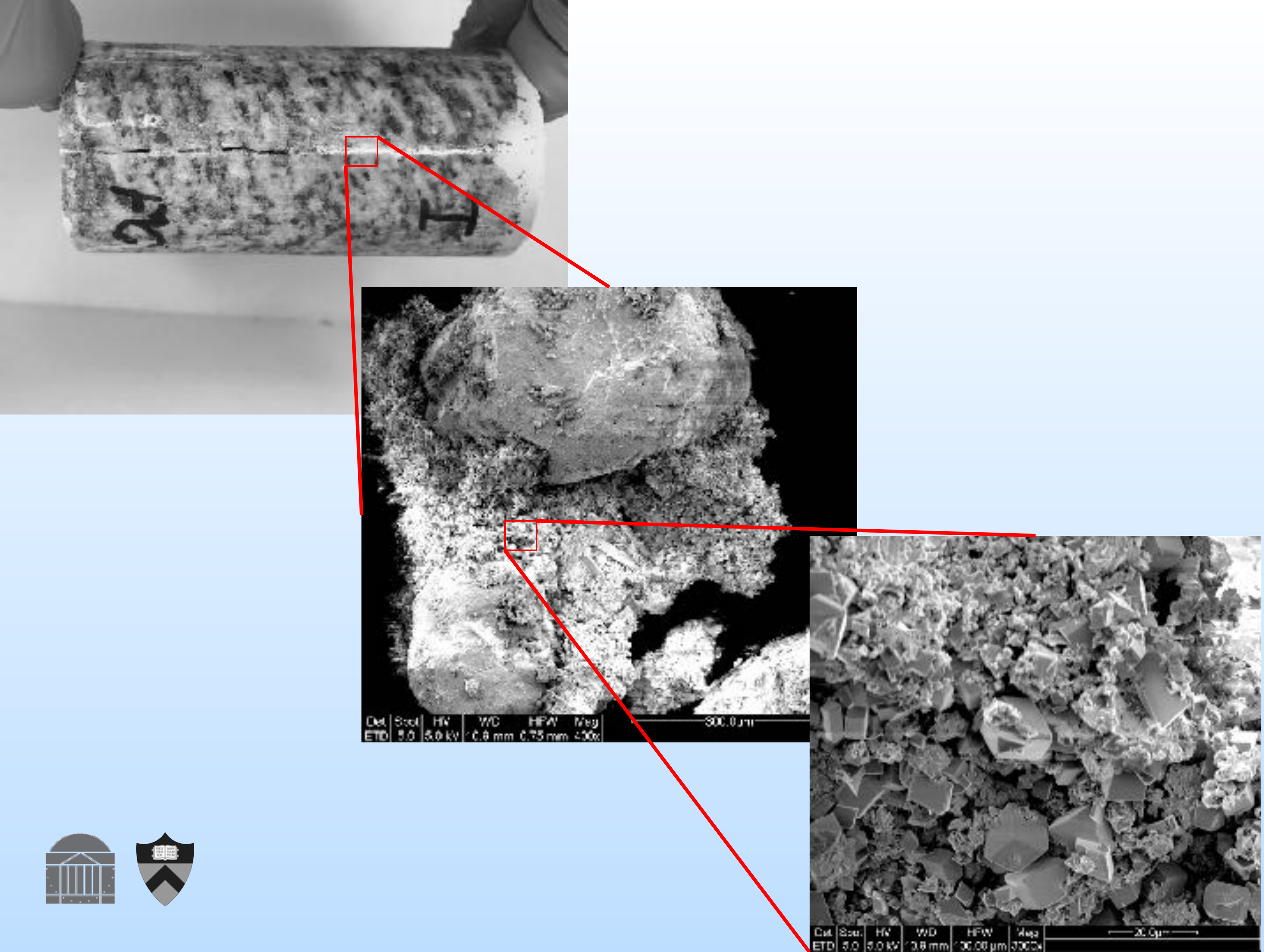
PDMAEMA polymer coating

- LCST: vary from 14 to 50°C in pure water (46°C 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 Spot HV WD HFW Mag
ETD 5.0 5.0 kV
500.0 µm
Det Spot HV WD HFW Mag
ETD 5.0 5.0 kV
20.0 µm

accomplishments to date

- Discovered secondary mineral phase precipitates in the psuedowollastonite/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 40ºC
- 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

lessons learned

- Psuedowollastonite reactivity very different than wollastonite
- The ability to precipitate something other than a carbonate appears to impart important properties from the standpoint of permeability reduction
- We have still not fully characterized the mechanism by which these precipitates form, but we are getting close
- Some CO_2 appears to be necessary but not too much
- Organic coating appear to work to limit reactivity, though not perfectly
- The resulting cements are effective at joining a fractured surface

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

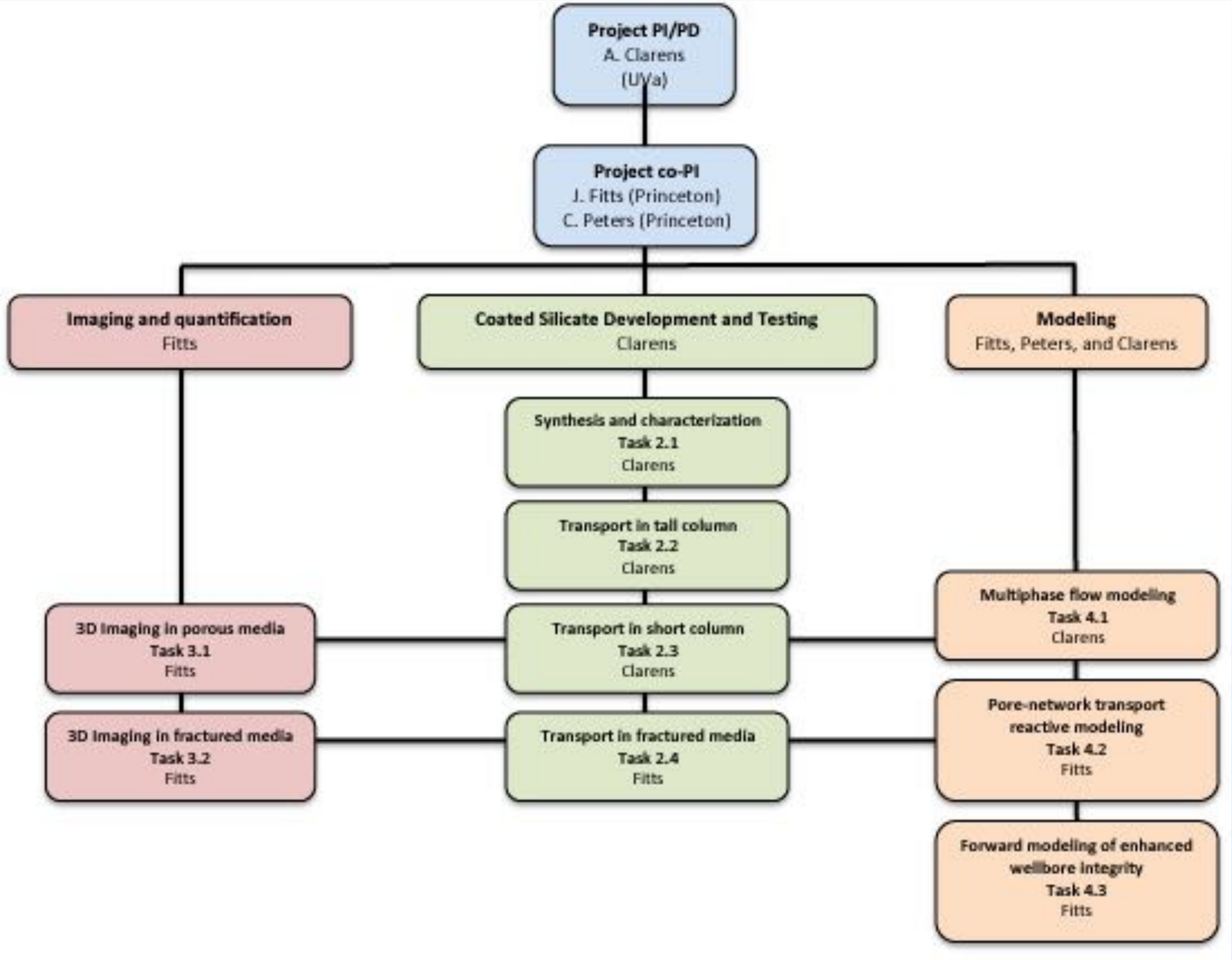
– The unanticipated formation of silicate hydrates, driven by the presence of low partial pressures of CO_2, could be an important step to producing stable cements

– Significant drops in permeability have been observed and these precipitates are very resistant to re-dissolution in the presence of CO_2.

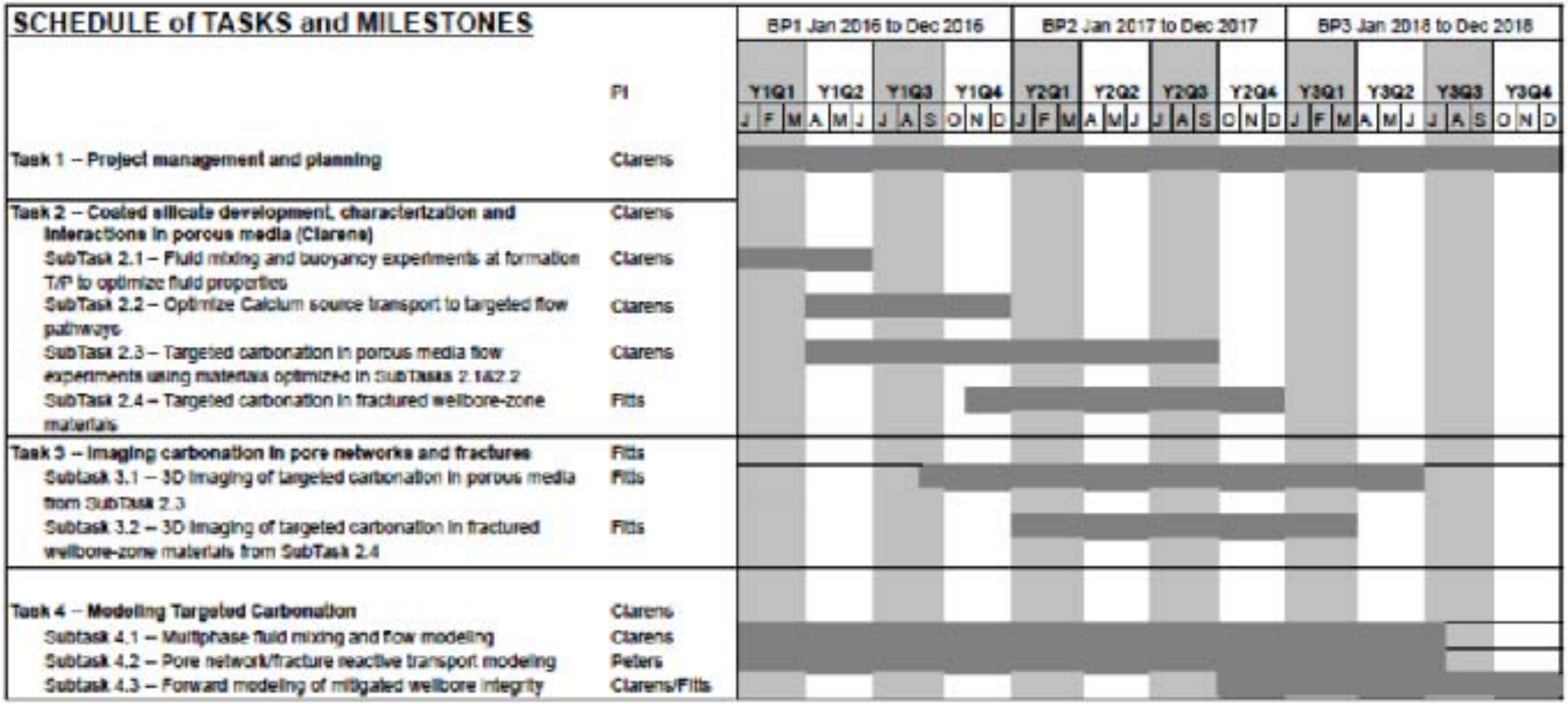
– Temperature sensitive coatings appear to be able to help us selectively deploy these materials at the desired depths

many thanks

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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