Targeted Mineral Carbonation to Enhance Wellbore Integrity

DE-FE0026582

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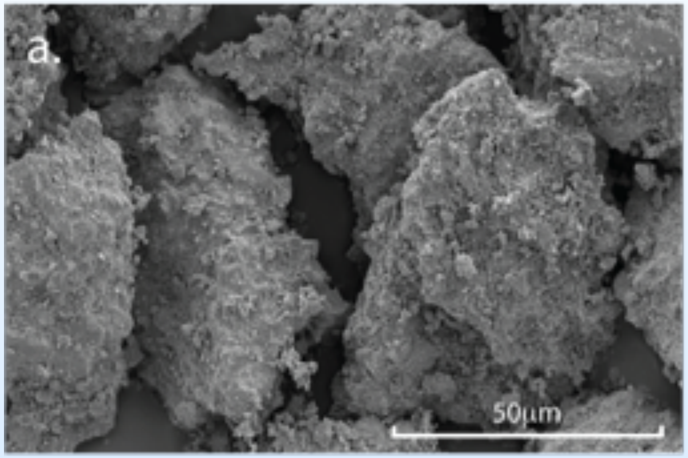
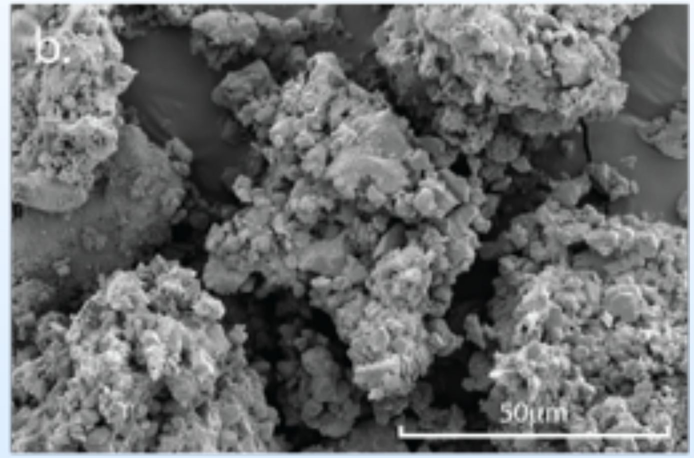
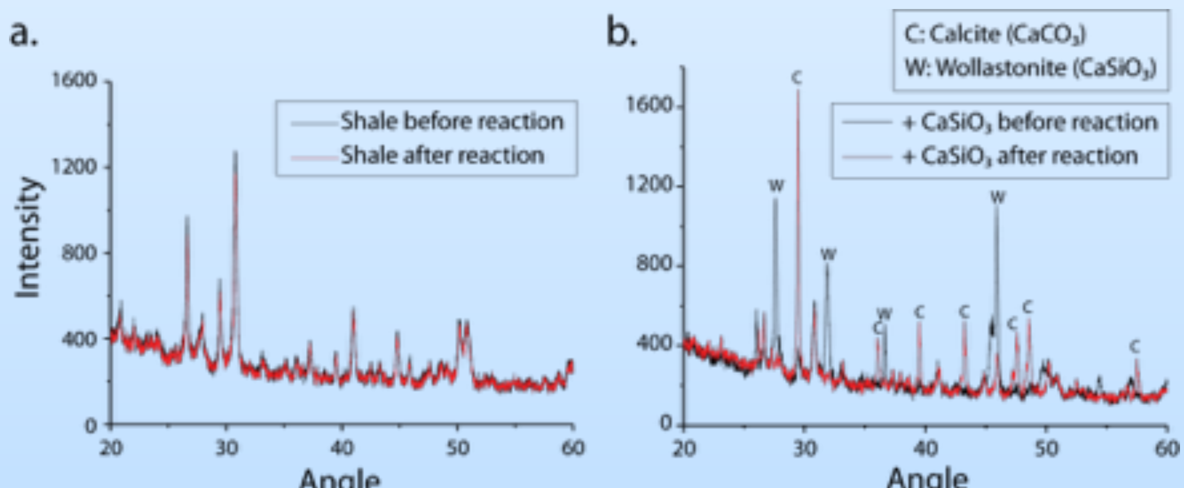
preface



shale grains



shale grains + CO_2 + $CaSiO_3$

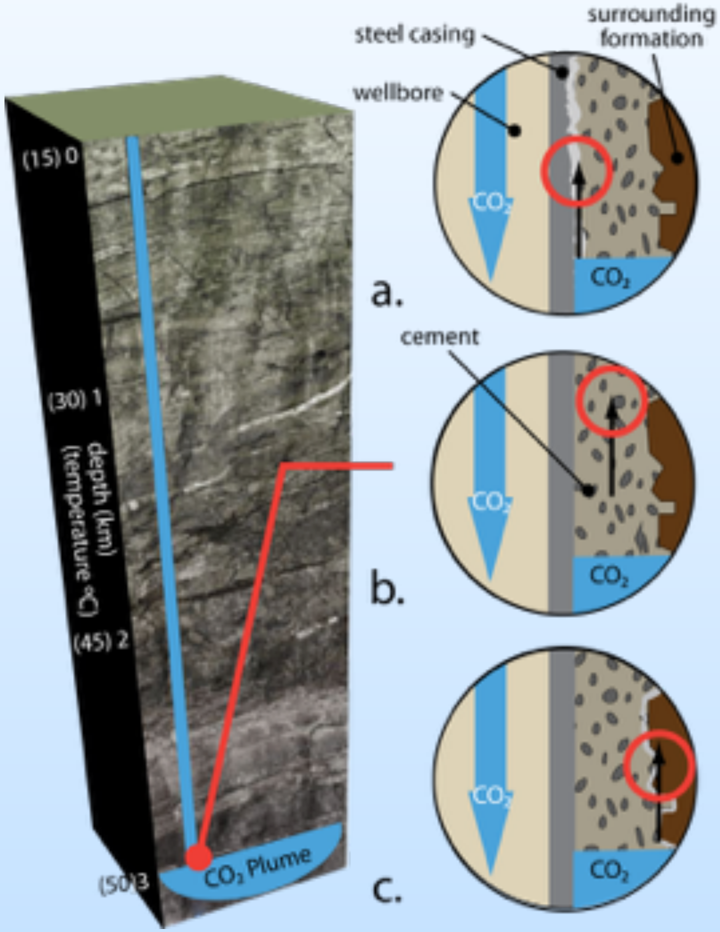


Tao, et al. (2016), Env. Eng. Sci., 10/16

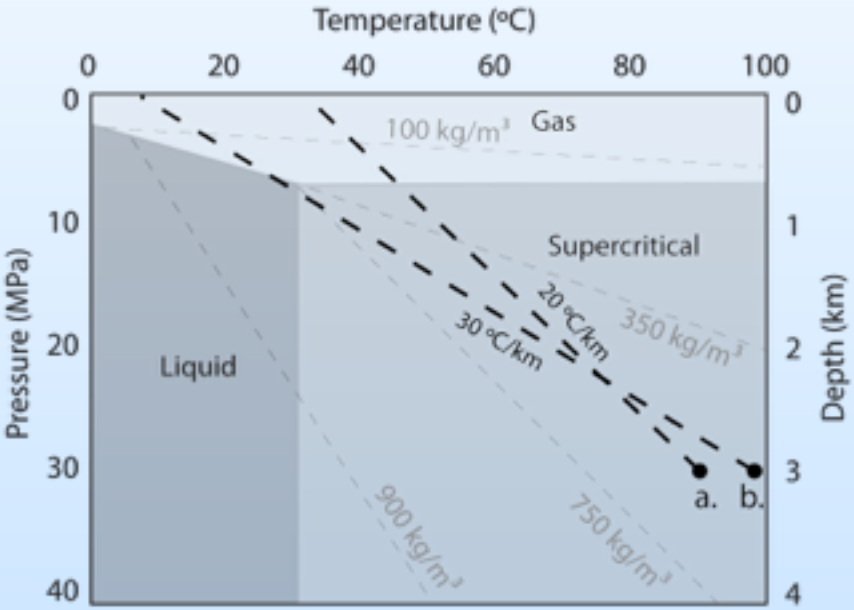
benefit to the program

- 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)

motivation



steel casing
surrounding formation
wellbore
cement
(15) 0
(30) 1
(45) 2
(50) 3
depth (km)
(temperature °C)
CO_2 Plume
CO_2
a.
b.
c.

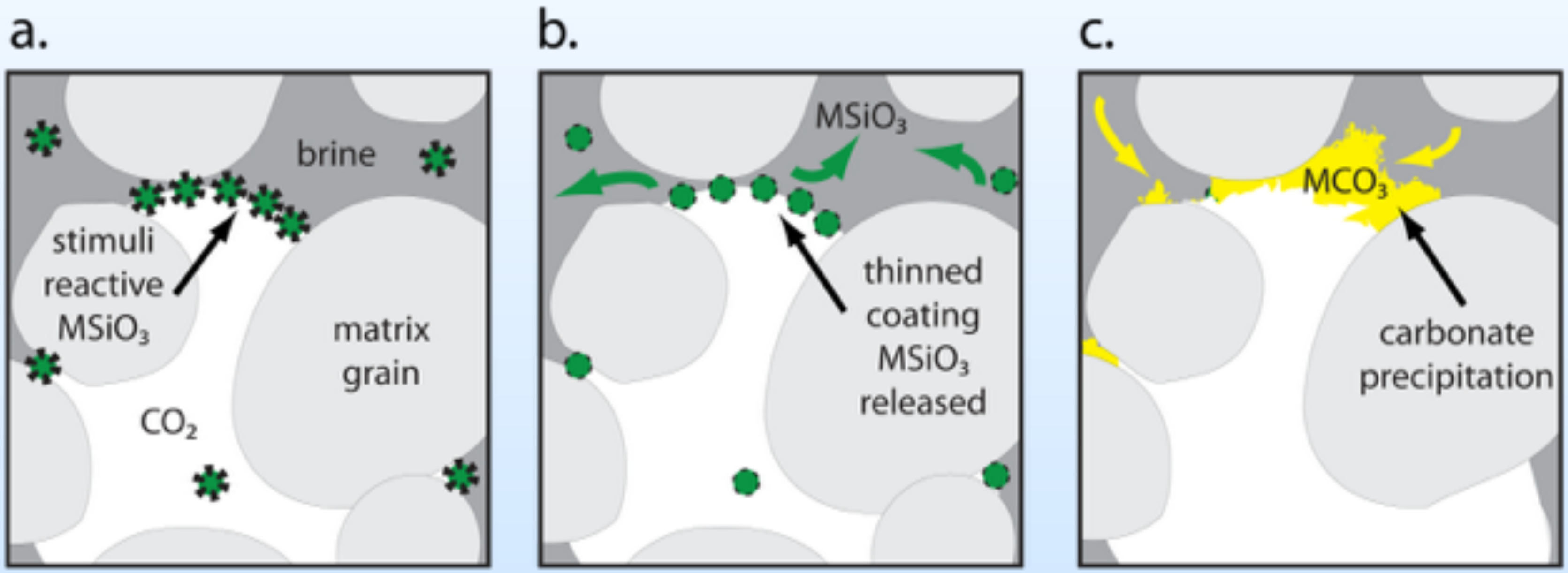


Temperature (°C)
0
20
40
60
80
100
Pressure (MPa)
Depth (km)
Gas
Liquid
Supercritical
100 kg/m³
350 kg/m³
750 kg/m³
900 kg/m³
20 °C/km
30 °C/km
a.
b.

project overview: goals and objectives

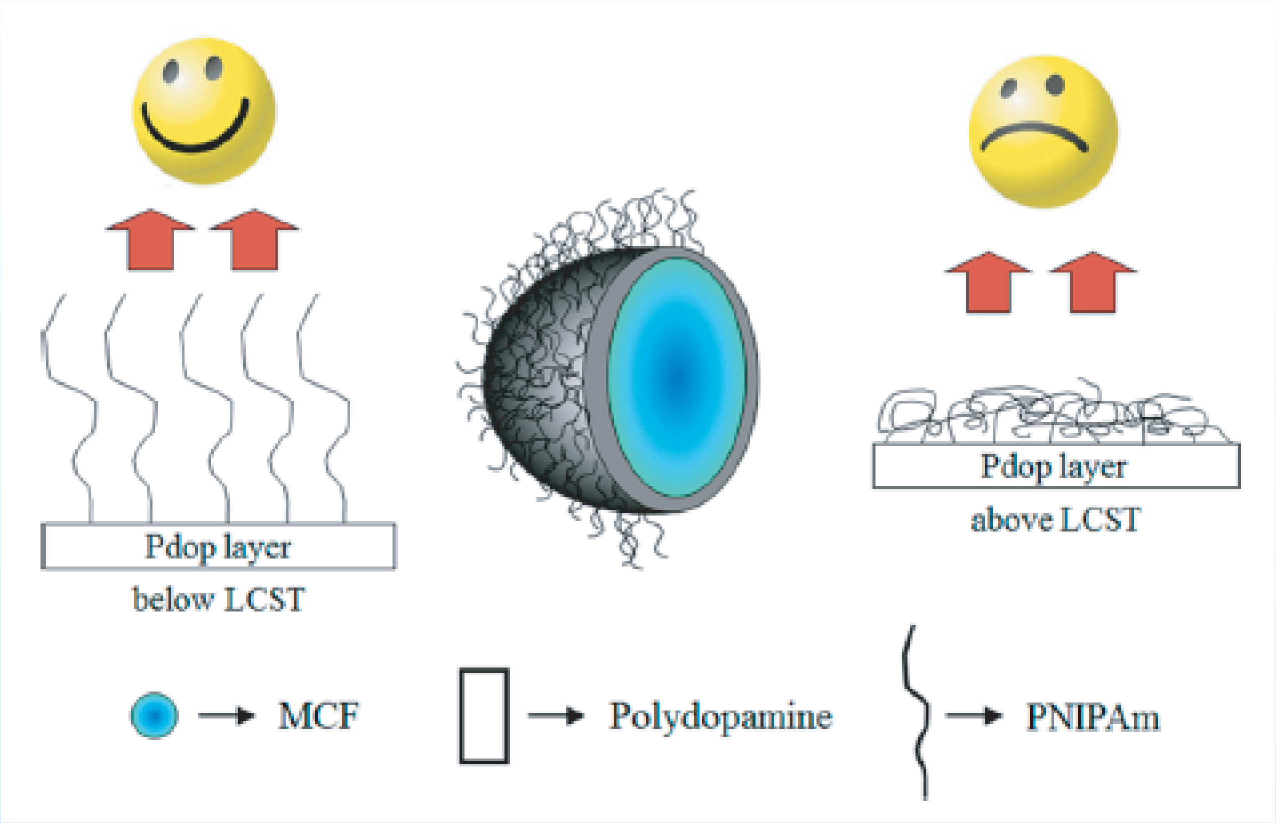
- Project management and planning
- Coated silicate development, characterization and interaction in porous media
  - Fluid mixing and buoyancy experiments at formation T/P to optimize material properties
  - Evaluate the performance of coated mineral silicates in packed columns
  - Targeted carbonation 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

motivation and underlying chemistry



$T > T_C$	$T < T_C$	$T < T_C$
$MSiO_3$ contained	$MSiO_3$ released	MCO_3 precipitated
Buoyancy flow	Buoyancy flow	Pores blocked, no flow

motivation and underlying chemistry

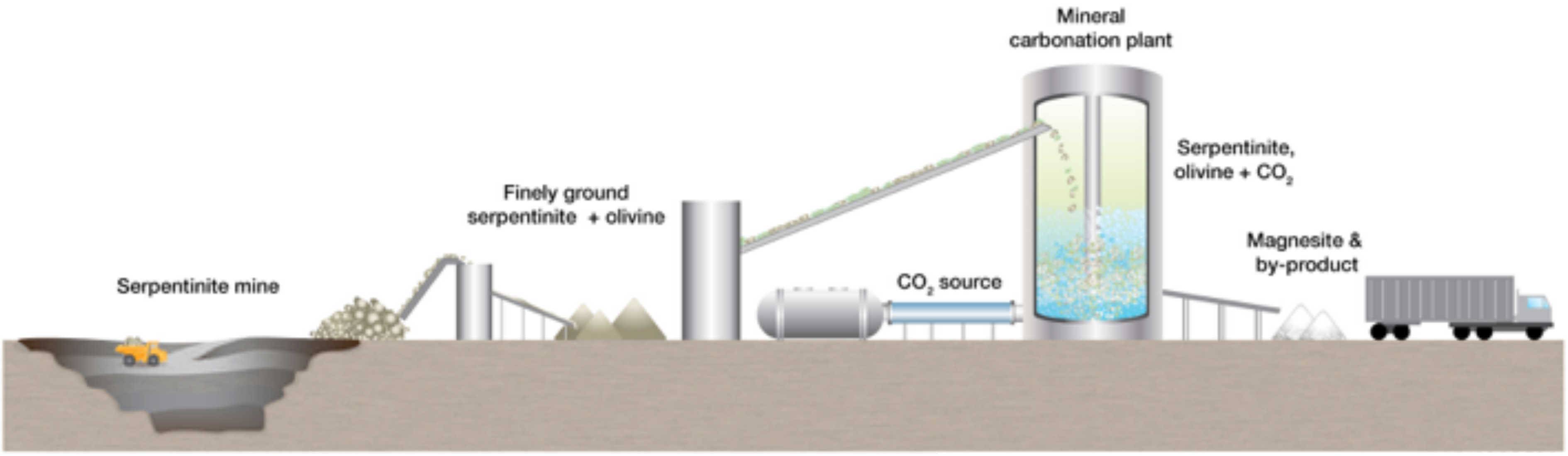


Ma et al. 2013

motivation and underlying chemistry

$$MSiO_{3(s)} + CO_{2(l,sc)} \rightarrow MCO_{3(s)} + SiO_{2(s)}$$

where M = Ca, Mg

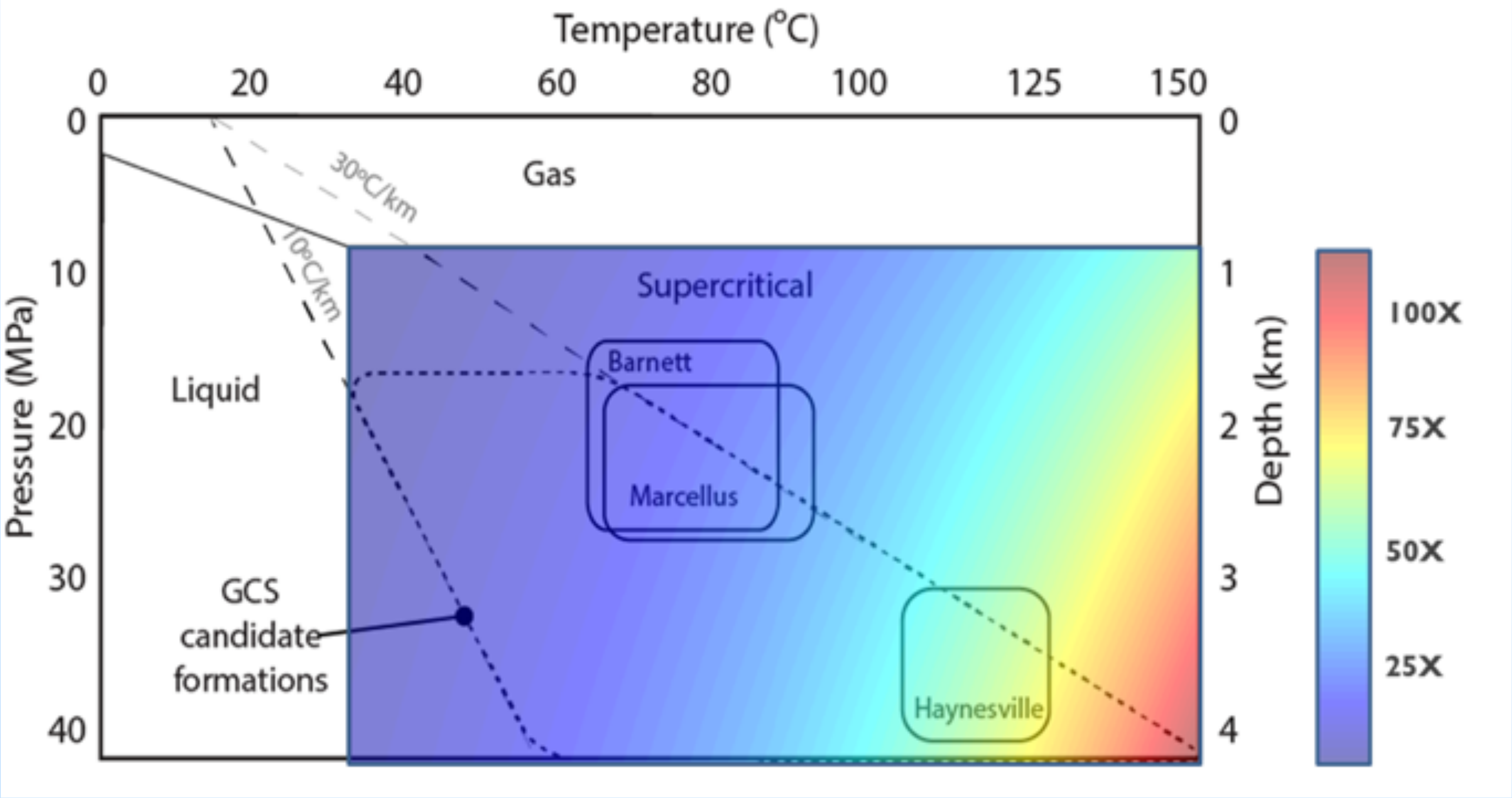


adapted from http://www.co2crc.com.au

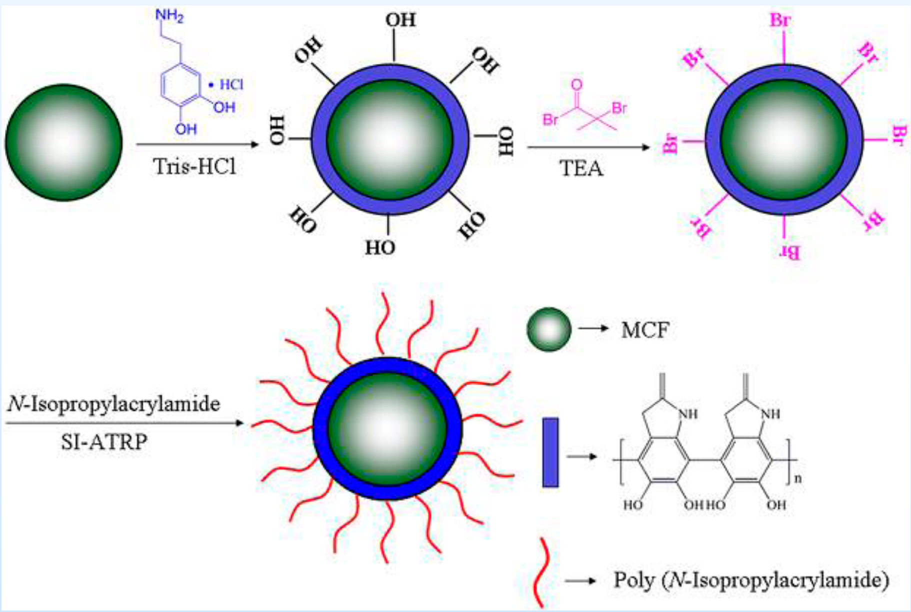
nanoparticle core

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

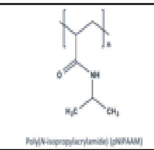
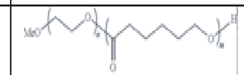
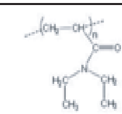
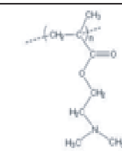
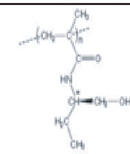
nanoparticle core



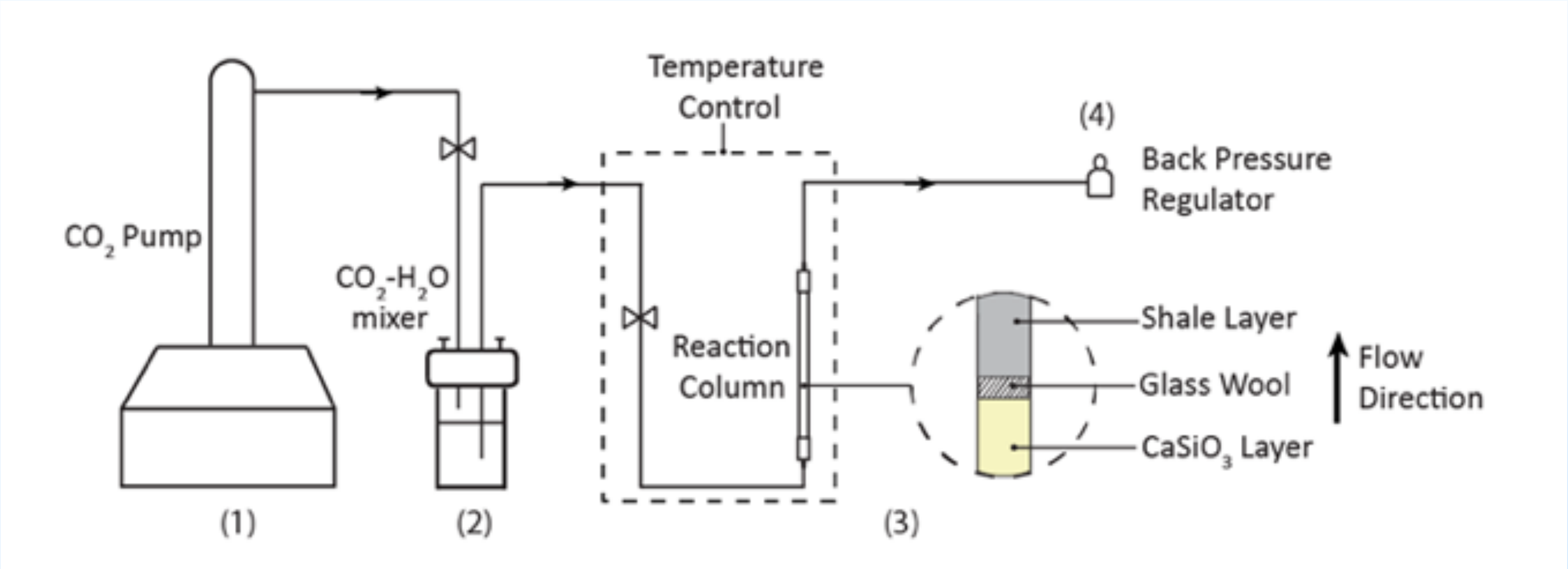
nanoparticle coating

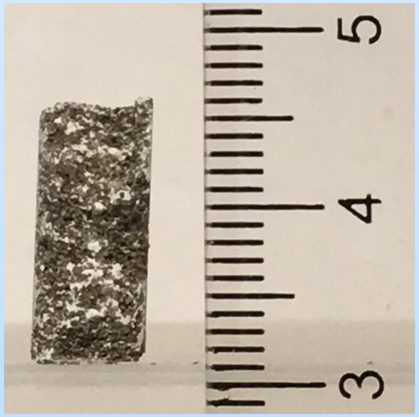


Ma et al. 2013

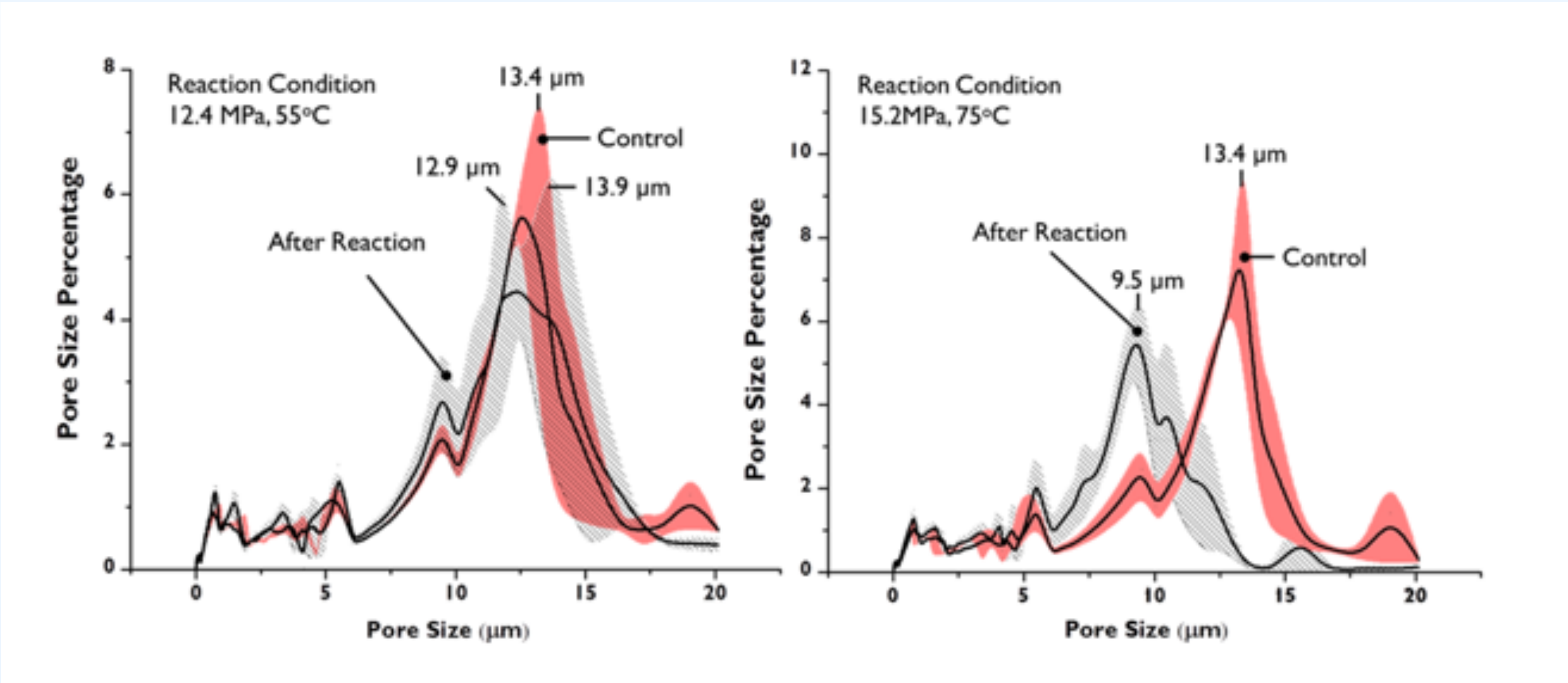
Polymer	Structure	LCST (°C)	Citation
pNIPAAM		32	Hugo Almeida, Maria Amaral et al. (2012)
PNVCL		33~39	Carolina Alarcon et al. (2005)
PEG-b-PNVCL		39	Ji Liu et al. (2014)
PDEAAm		26~35	Hugo Almeida, Maria Amaral et al. (2012)
PDMAEMA		50	Kang Moo Huh, et al. (2000)
Poly[N-(L) (hydroxymethyl)propylmethacrylamide]		30	Hugo Almeida, Maria Amaral et al. (2012)
PEO/PPO		32~35	Z. Ma, X. Jia et al (2013)
PEO-PPO-PEO	$HO\text{-}(CH_2CH_2O)_x\text{-}(CH_2\overset{CH_3}{\overset{\vert}{C}}HO)_y\text{-}(CH_2CH_2O)_x\text{-}H$	35~38	Martien a. Cohen stuart et al. (2010)
PEG-PLA-PEG		35~38	Zhibing Hu et al. (2010)
POEGMA188		26	Zhibing Hu et al. (2010)

experimental setup

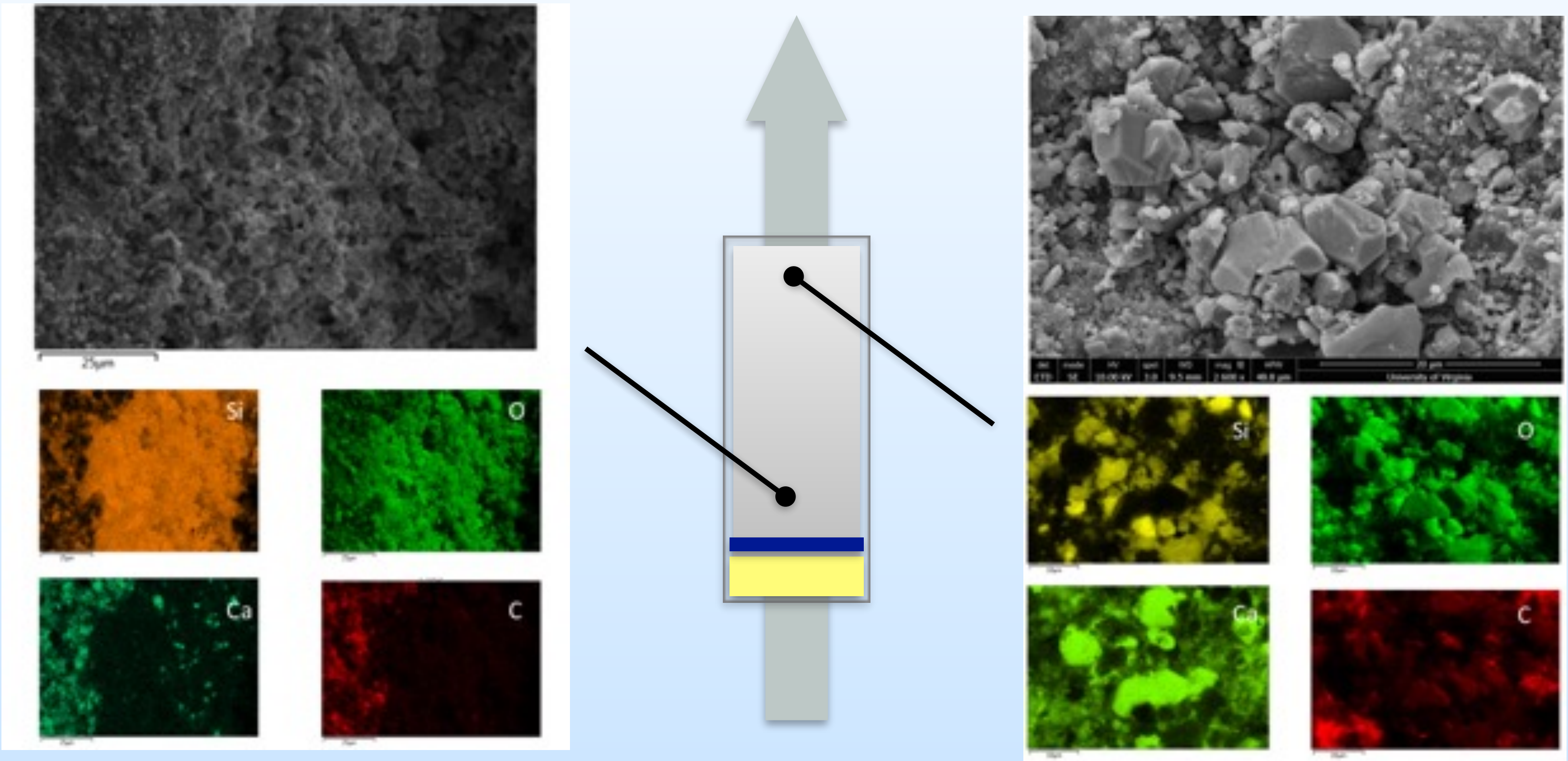




mercury intrusion porosimetry



precipitate relationship to flow



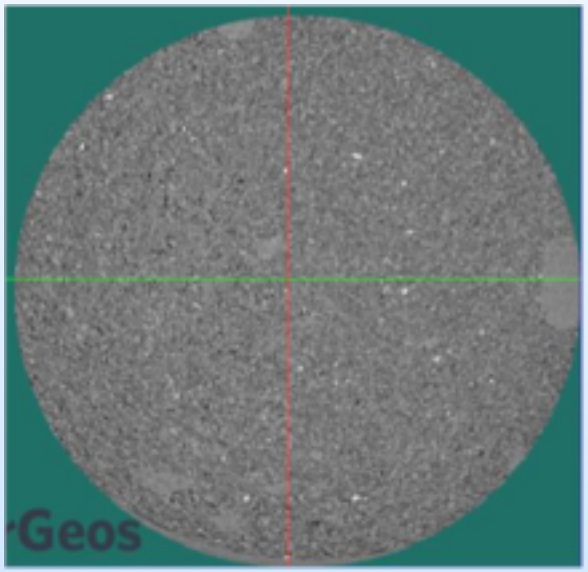
close to inlet

$CO_2 + H_2O$

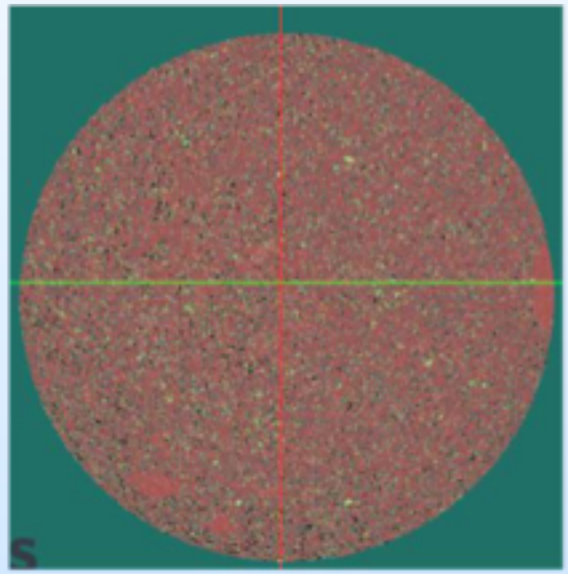
close to outlet

$$CaSiO_3 + CO_2 = CaCO_3 + SiO_2$$

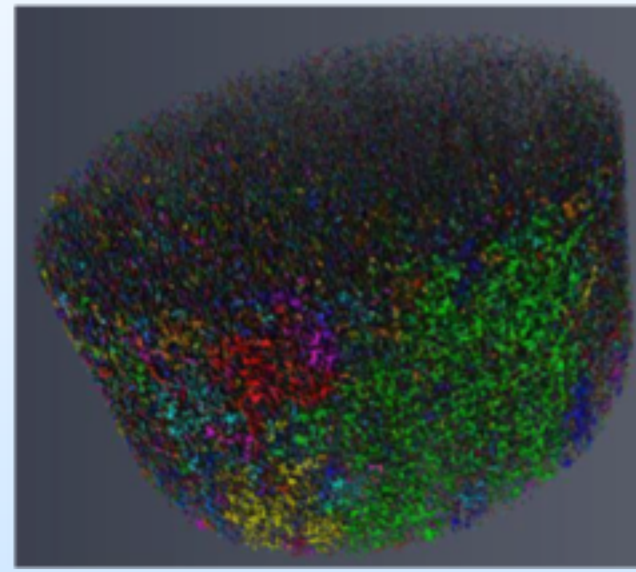
synchrotron xCT images of columns



2D grey scale

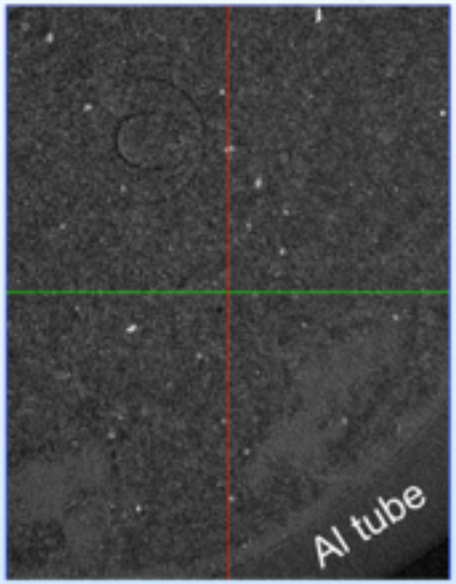


segmented 2D slice

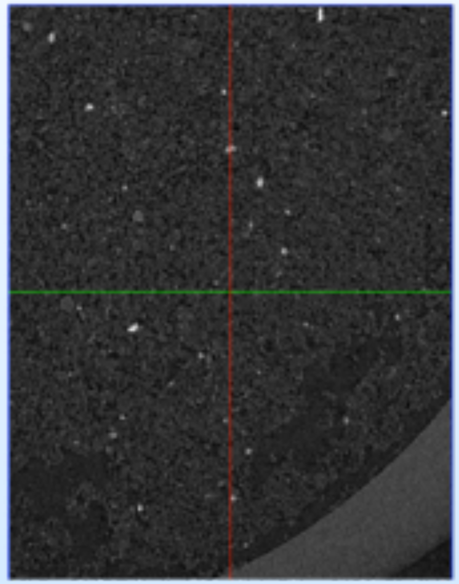


3D volume
colors depict
connectivity

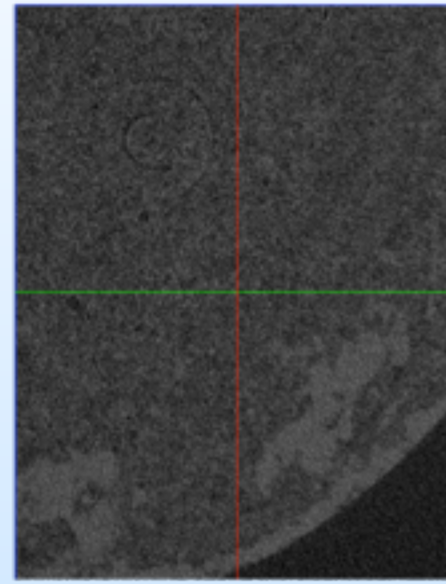
synchrotron xCT images of columns



2D grey scale slice collected above the Xe k-edge



below the Xe k-edge

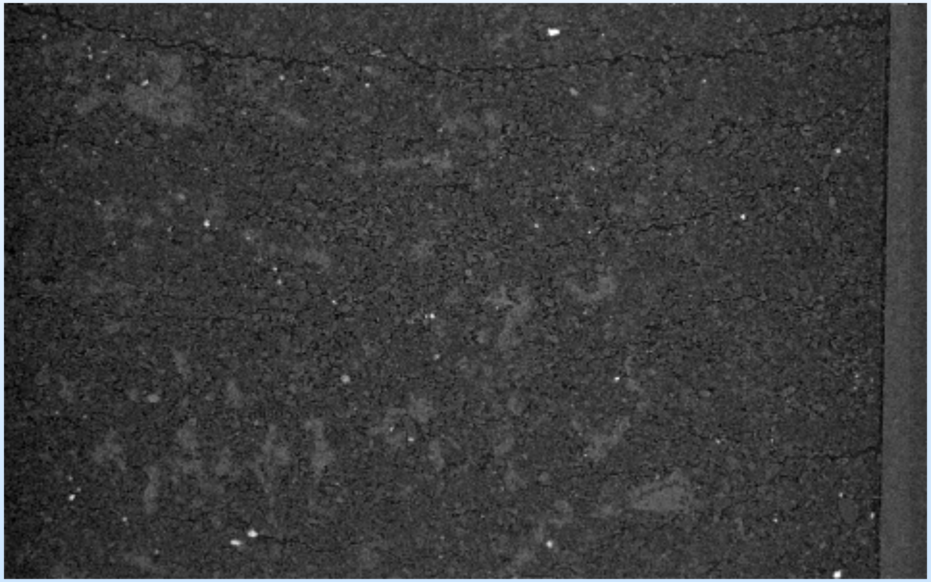


the subtracted image

synchrotron xCT images of columns

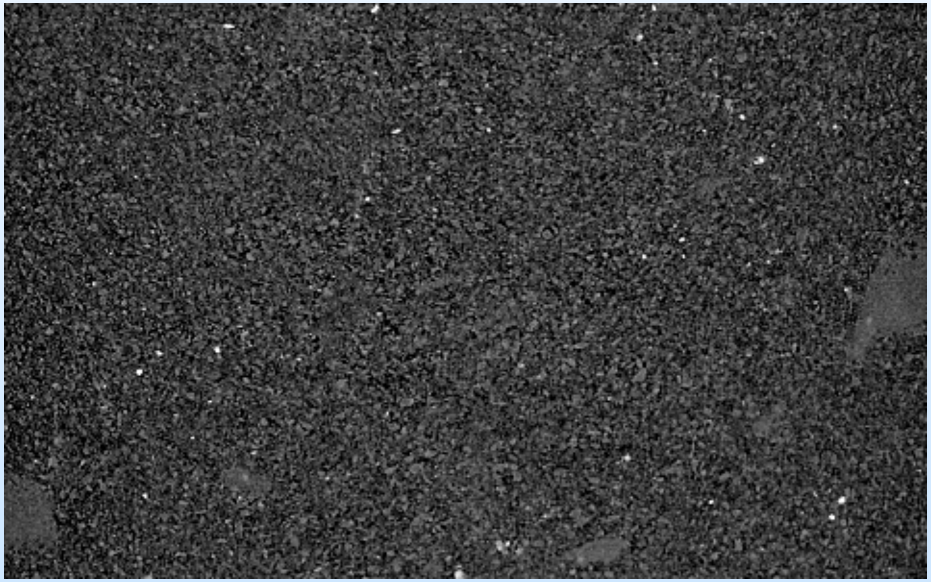
15.5 MPa, 95°C, Wollastonite:Shale = 20:80, flow rate = 0.1 ml/min

before reaction



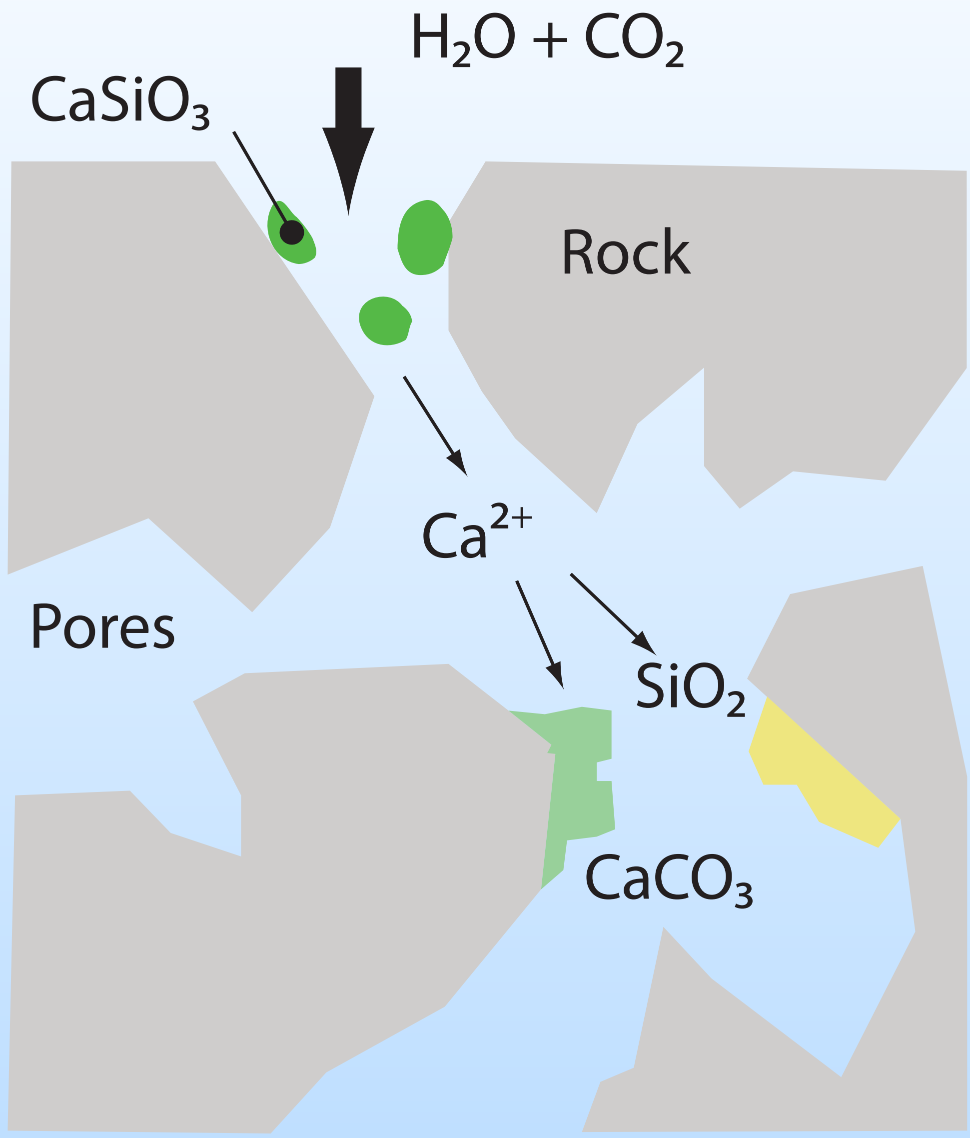
SiO_3 particles visible

after reaction

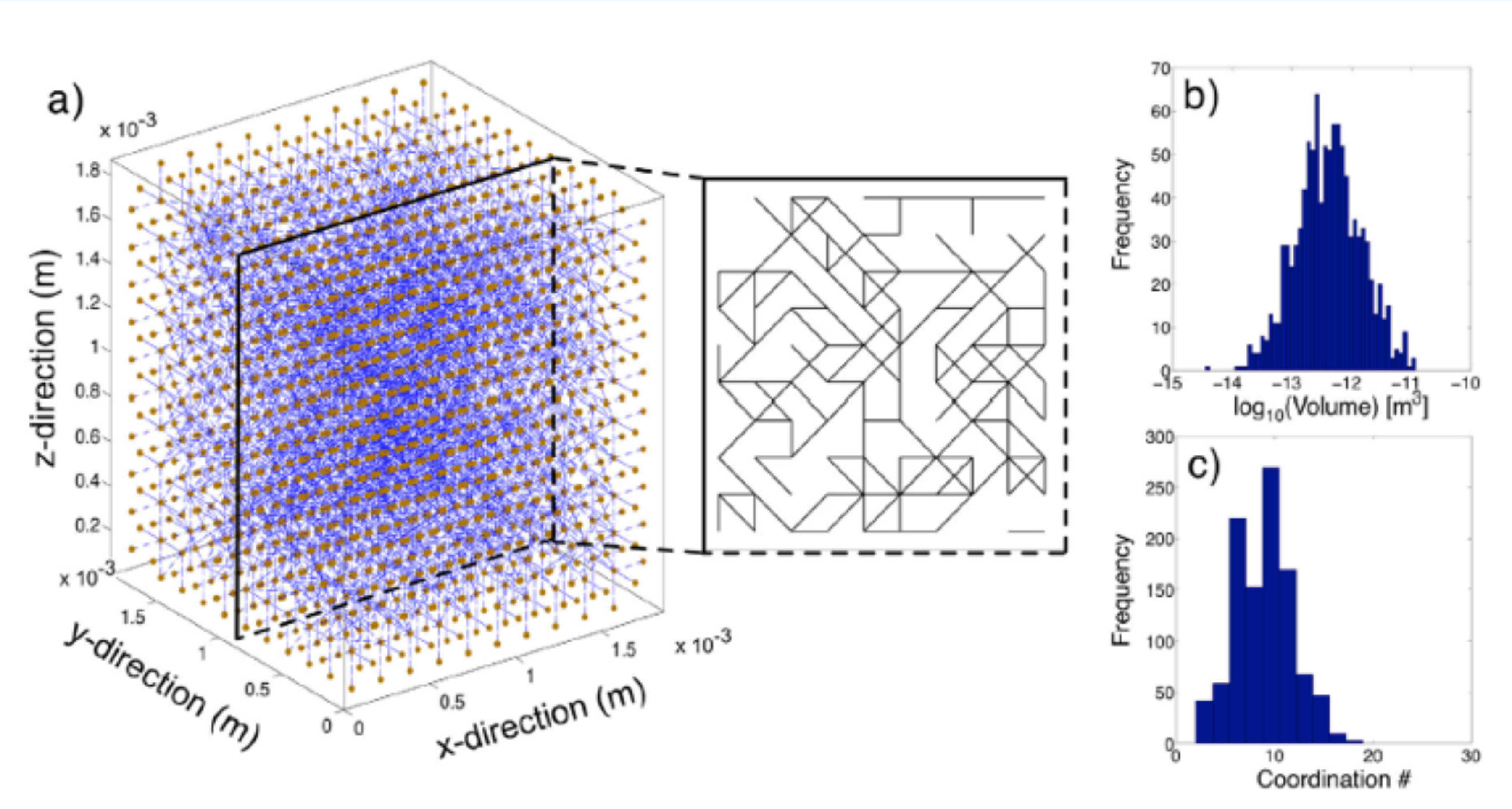


SiO_3 particles mostly dissolved creating new pores, some of matrix cemented

pore network modeling



pore network modeling



(2013), Water Resour. Res., 49, 6006–6021

pore network modeling

- Flow field

$$\sum_{j}^{N_i} Q_{ij} = \sum_{j}^{N_i} G_{ij} \frac{p_i - p_j}{L_{ij}} = 0$$

the subscripts i and ij denote the pore body and pore throat
Qij [L3/T] is the volumetric flow rate of water from pore body i to j
Gij [L5T/M] is the pore throat conductivity
p [M/LT2] is the water pressure at pore body
Ni is the number of pore throats connected to pore body i,
Lij [L] is the pore throat length

- Species

$$V_i^0 (1 - \varepsilon_{ij}^c) \frac{dC_i^m}{dt} = -C_i^m \sum_{j}^{N_i} max(Q_{ij}, 0) - \sum_{j}^{N_i} min(Q_{ij}, 0) - \sum_{j}^{N_i} (D_{ij}^w A_{ij}^w) \frac{C_i^m - C_{ij}^m}{L_{ij}/2} + V_i^0 R_i^m$$

- Solid phase volume fractions

$$V_{i/ij}^0 \rho^s \frac{\varepsilon_{i/ij}^s}{dt} = V_{i/ij}^0 R_{i/ij}^s$$

m denotes the species
C is the species mass/molar concentration
ε is the calcite volume fraction
Vo [L3] is the volume of pore body in the absence of calcite
Dwiij [L2/T] is the species dispersivity in water phase
Aw and Af ij ij ij [L2] are the cross-sectional areas of water phase and calcite in the pore throat
R is the sink/source term

- Calcite precipitation/dissolution

$$r_{prec/diss} = \beta(k_1 a^{H+} + k_2 a^{H_2CO_3} + K_3) \left(1 - \frac{a^{Ca^{2+}} a^{CO_3^{2-}}}{K_{sp}}\right)^{n_p} S^c$$

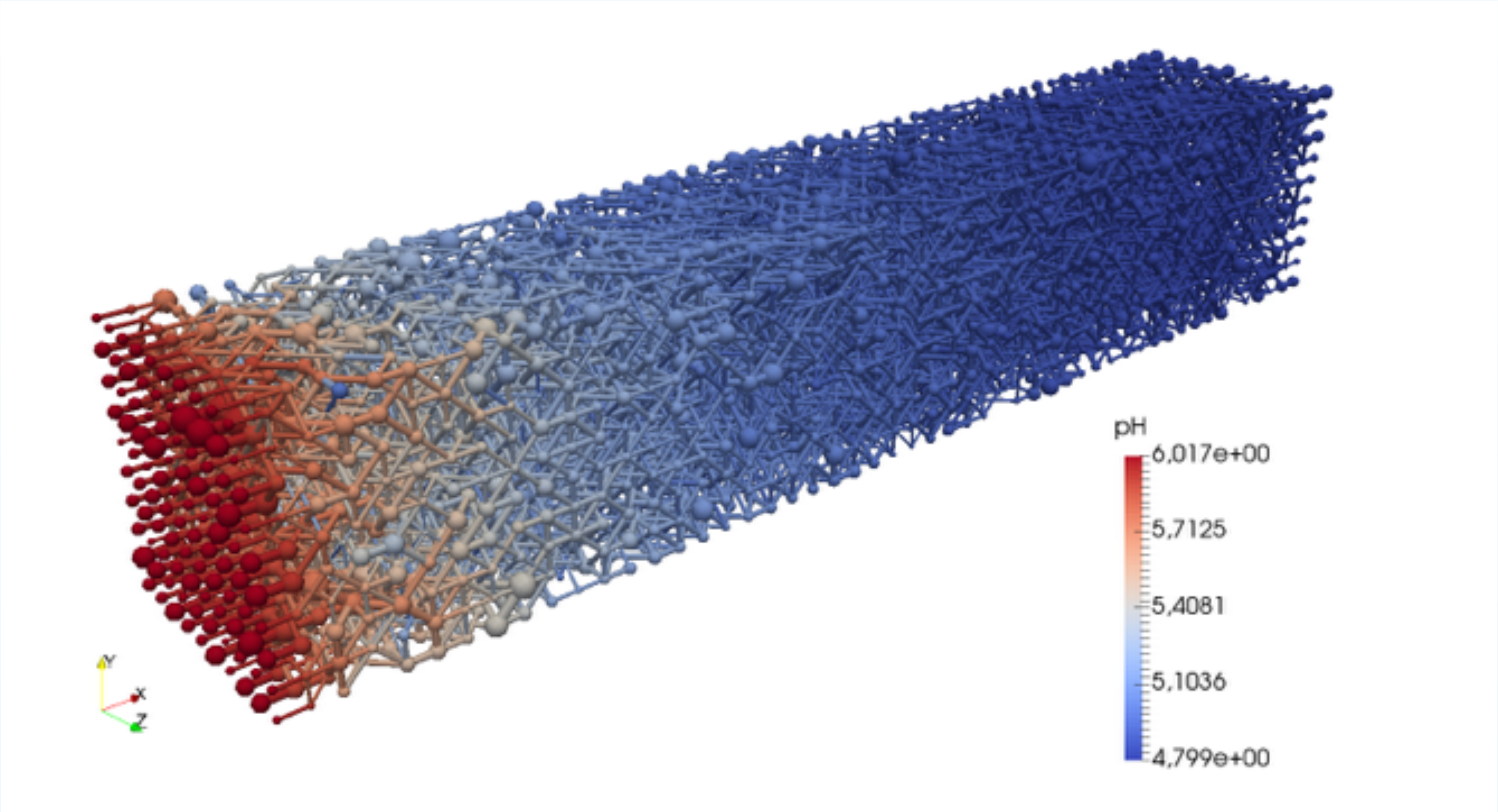
k1 , k2 , and k3 are the reaction rate constants
a is the species activity
Ksp is the solubility of product of calcite
np is an empirical parameter
Sc is the available specific area for calcite precipitation in a pore element

- Source/sink

$$R^s = -r_{prec/diss} M^s$$

Ms is the molecular weight of solid phase

preliminary results



accomplishments to date

- Synthesized wollastonite nanoparticles (10s of nm to µms)
- Synthesized coatings with a LCST of 25ºC
- Measured permeability change in packed columns reacted with uncoated wollastonite
- Obtained xCT images of columns at APS
- Processed data using segmentation analysis to measure connectivity of pores
- Imaged cores using µCT at UVa
- Used SEM and EDS to begin exploring connections between flow and precipitation
- Developed pore network modeling framework

synergy opportunities

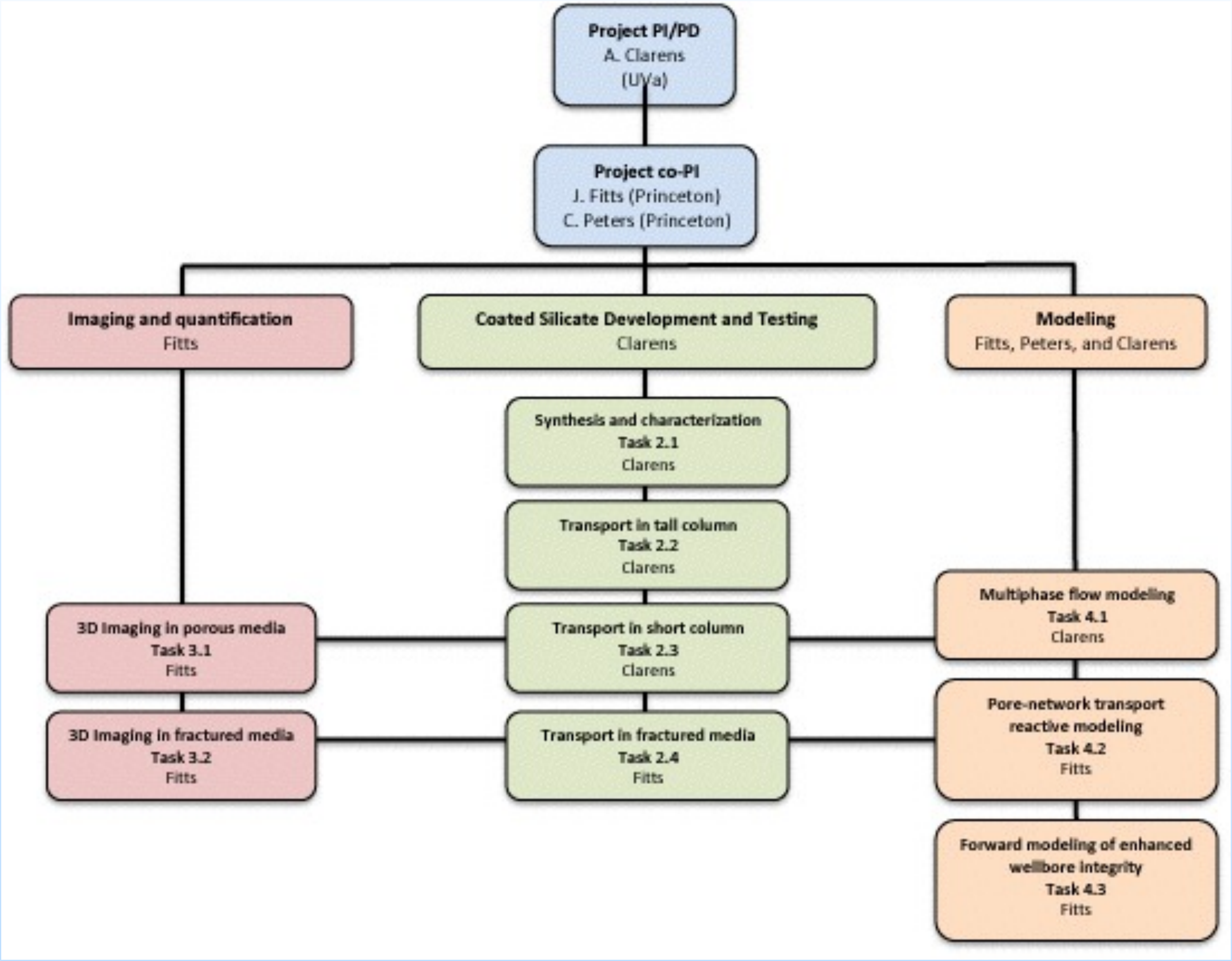
- w/ other PIs in this program:
  - Experience with nanoparticles use in fractures and porous media
    - Functionalization
    - Transport
    - Modeling
- w/ other PIs in Basalt storage area:
  - Reaction of carbonates in high P_{CO2} environments where the interplay between dissolution and precipitation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

summary

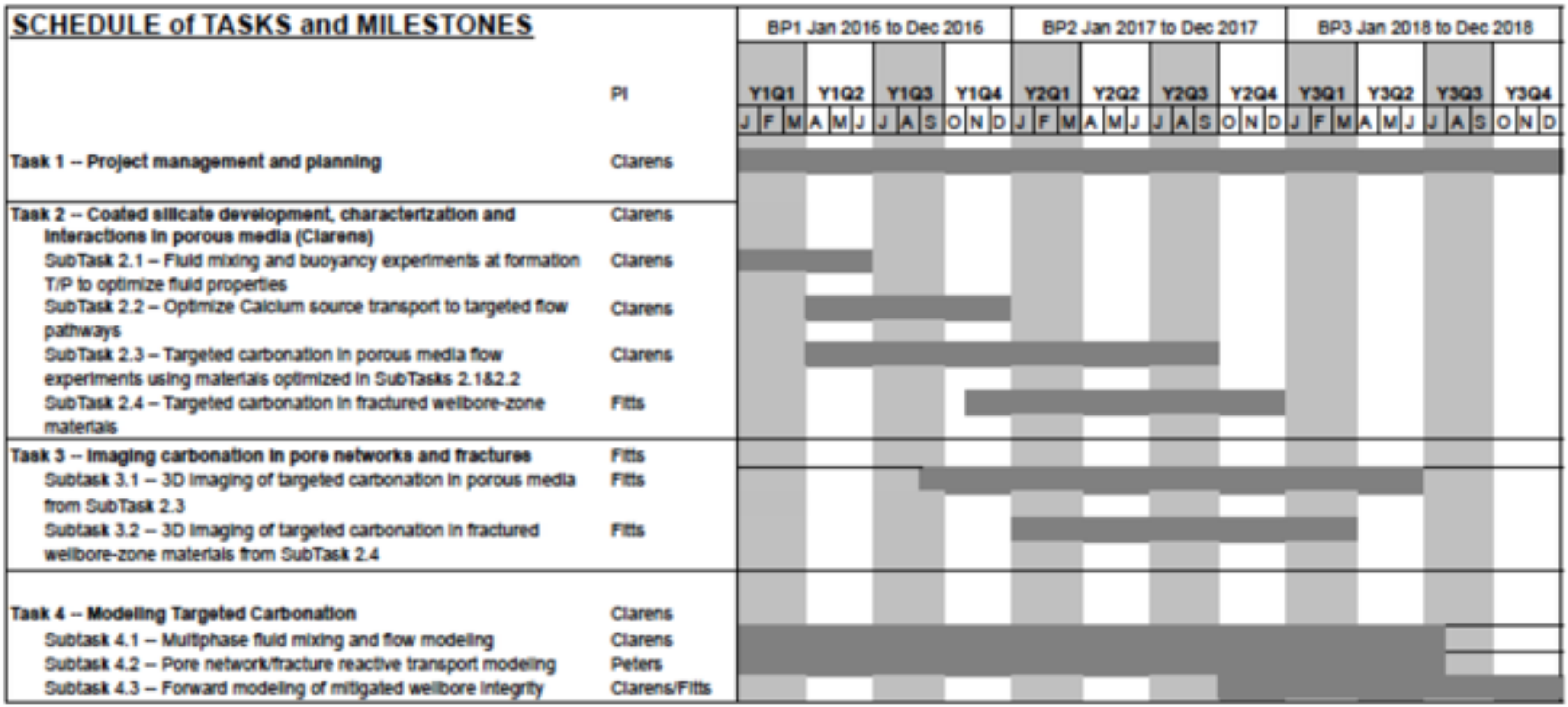
- Mineral silicates can be used to cement porous media and reduce its permeability when delivered as nanoparticles and exposed to a high P_{CO2} environment
- These reactions would leverage the favorable kinetic conditions of the deep subsurface
- Our focus on developing temperature sensitive coatings is to control the location (depth) where these reactions occur
- Ongoing experiments are showing the temperature sensitivity of these functionalized nanoparticles
- The carbonation of these silicates and precipitation of the carbonates is dependent on both CO_2 concentration (as a reactant) and $H_2CO_3^*$ (as an acid)
- Models are being developed to help us optimize the conditions under which maximum carbonation will occur

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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Appendix