Lenfest Center for Sustainable Energy
EARTH INSTITUTE | COLUMBIA UNIVERSITY

COLUMBIA UNIVERSITY
IN THE CITY OF NEW YORK

Geo-Chemo-Mechanical Studies for Permanent Storage of CO_2 in Geologic Formations
DE-FE0002386

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Presentation Outline

- **Benefit and Overview**
- **Results and Accomplishments**
  - Mineral Characterization
  - Effect of Temperature, Pressure and Chemical Additives on Mineral Carbonation
  - Changes in Pore Structure and Morphology due to Carbonation
  - Reactive Cracking
- **Summary**

Benefit of the Program

- Identify the program goals being addressed

Develop technologies to demonstrate that 99 percent of injected CO_2 remains in the injection zones surface area.

- Project Benefits

The project is to identify the effect of in-situ carbonation on the stability of geologic formations injected with CO_2. The technology, when successfully demonstrated, will provide valuable information on the stability of the CO_2 geological storage. This technology contributes to the Carbon Storage Program’s effort of ensuring 99 percent CO_2 storage permanence in the injection zone(s).

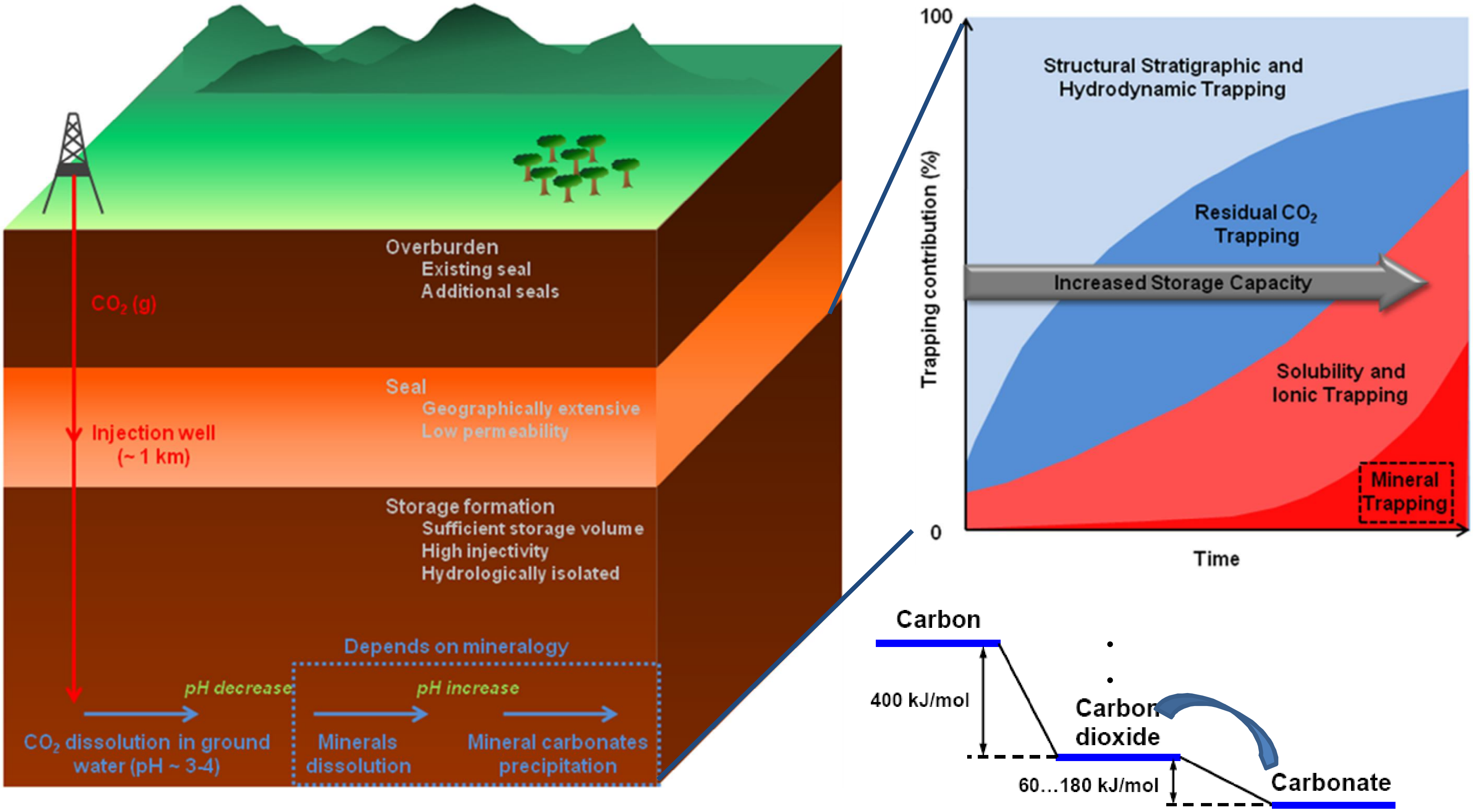
Project Overview: Goals and Objectives

(i) Determine and compare the effect of temperature, partial pressure of CO_2 and chemical additives on carbonation of various minerals such as olivine, labradorite, anorthosite and basalt

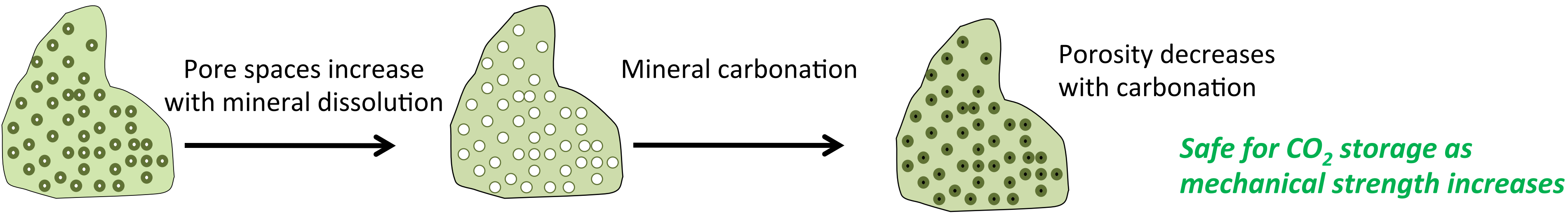
(ii) Quantify changes in pore structure and particle size before and after carbonation and analyze changes in morphological structure of the mineral due to carbonation

(v) Determine the effect of pore fluid chemistry on mechanical behavior of rocks such as changes in hydrostatic compaction and strain on thermally cracked dunite saturated with CO_2-saturated brines

Carbon Storage in Geologic Formations



Mineral Carbonation and Reactive Cracking

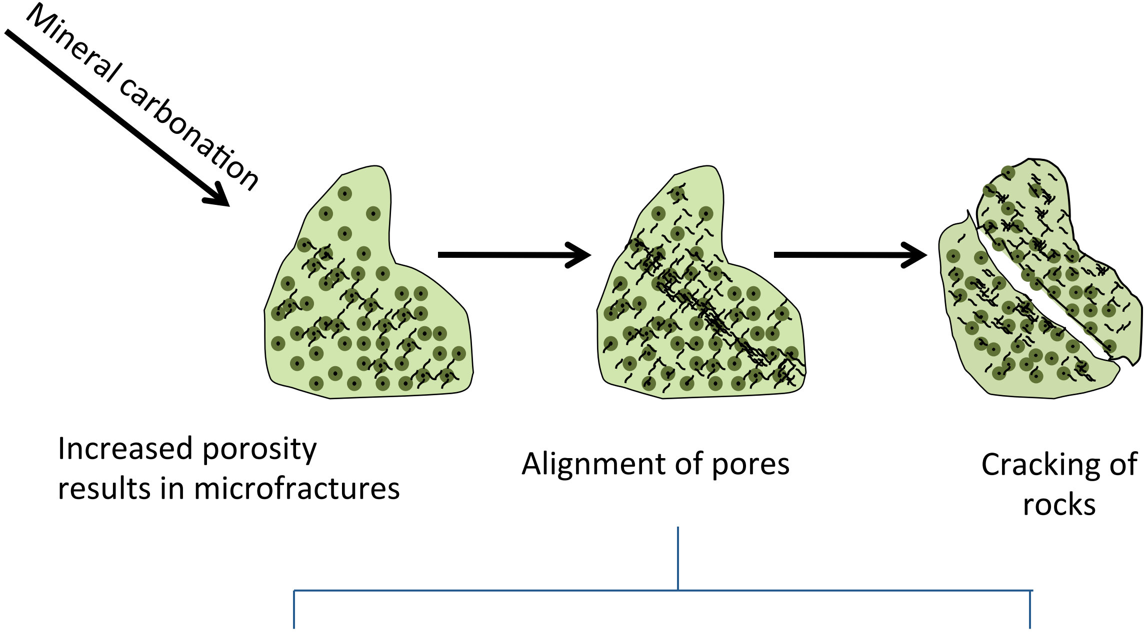


Pore spaces increase with mineral dissolution

Mineral carbonation

Porosity decreases with carbonation

Safe for CO_2 storage as mechanical strength increases



Mineral carbonation

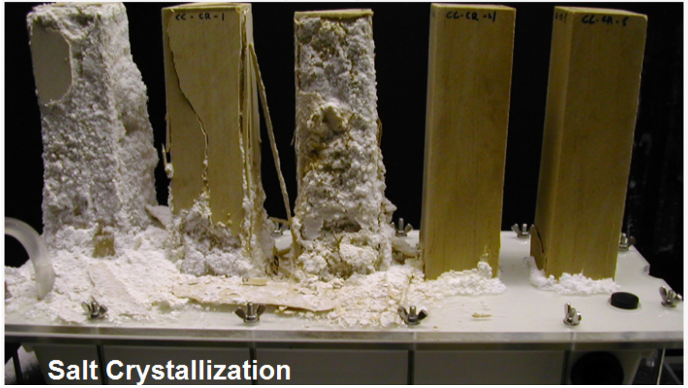
Increased porosity results in microfractures

Alignment of pores

Cracking of rocks

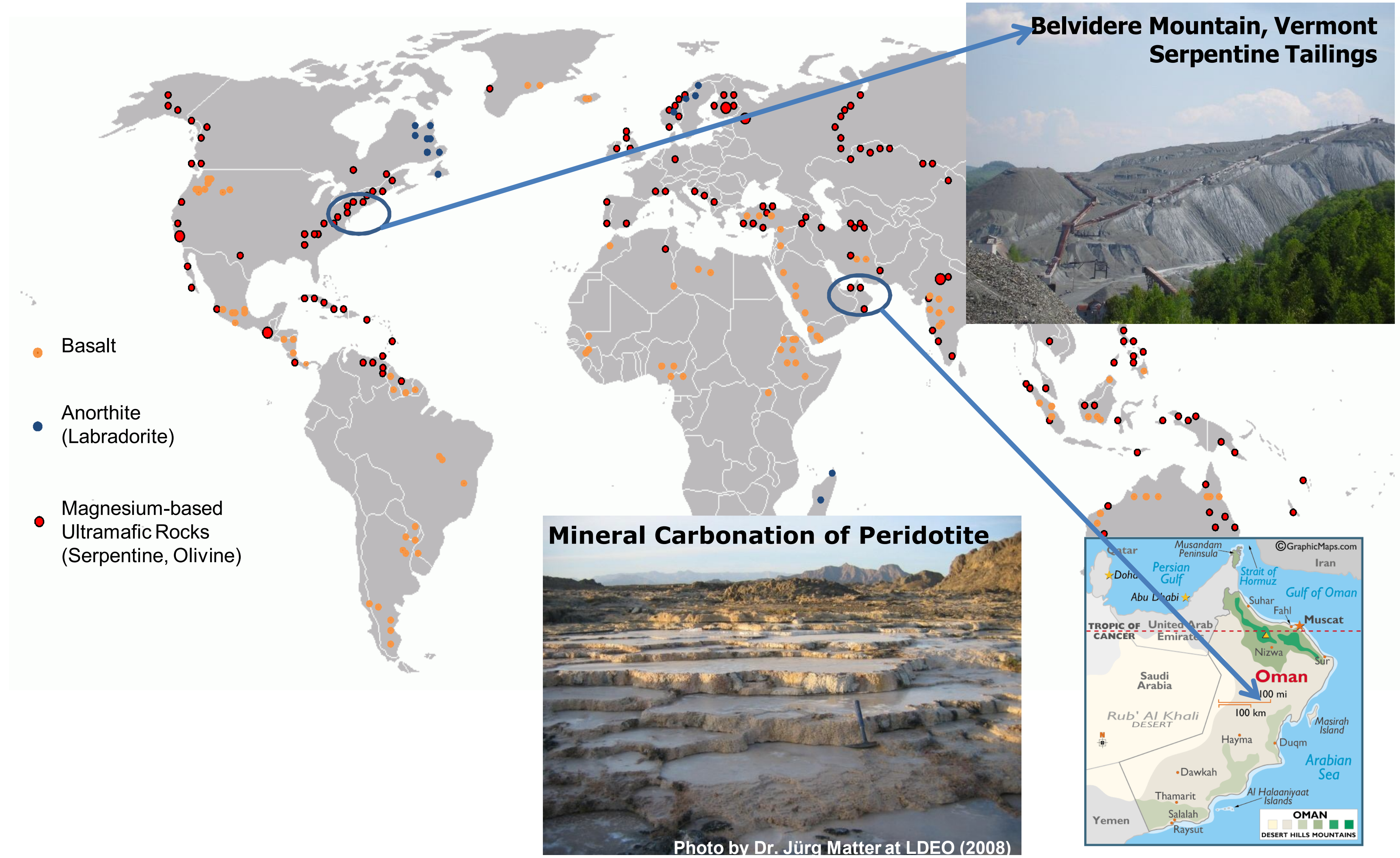
If overburden and caprock seal is good, then cracking is ok

If overburden and caprock seal is not good, is there a problem?



http://gwsgroup.princeton.edu/SchererGroup/Salt_Crystallization.html

Worldwide Availability of Minerals



Belvidere Mountain, Vermont
Serpentine Tailings

Mineral Carbonation of Peridotite

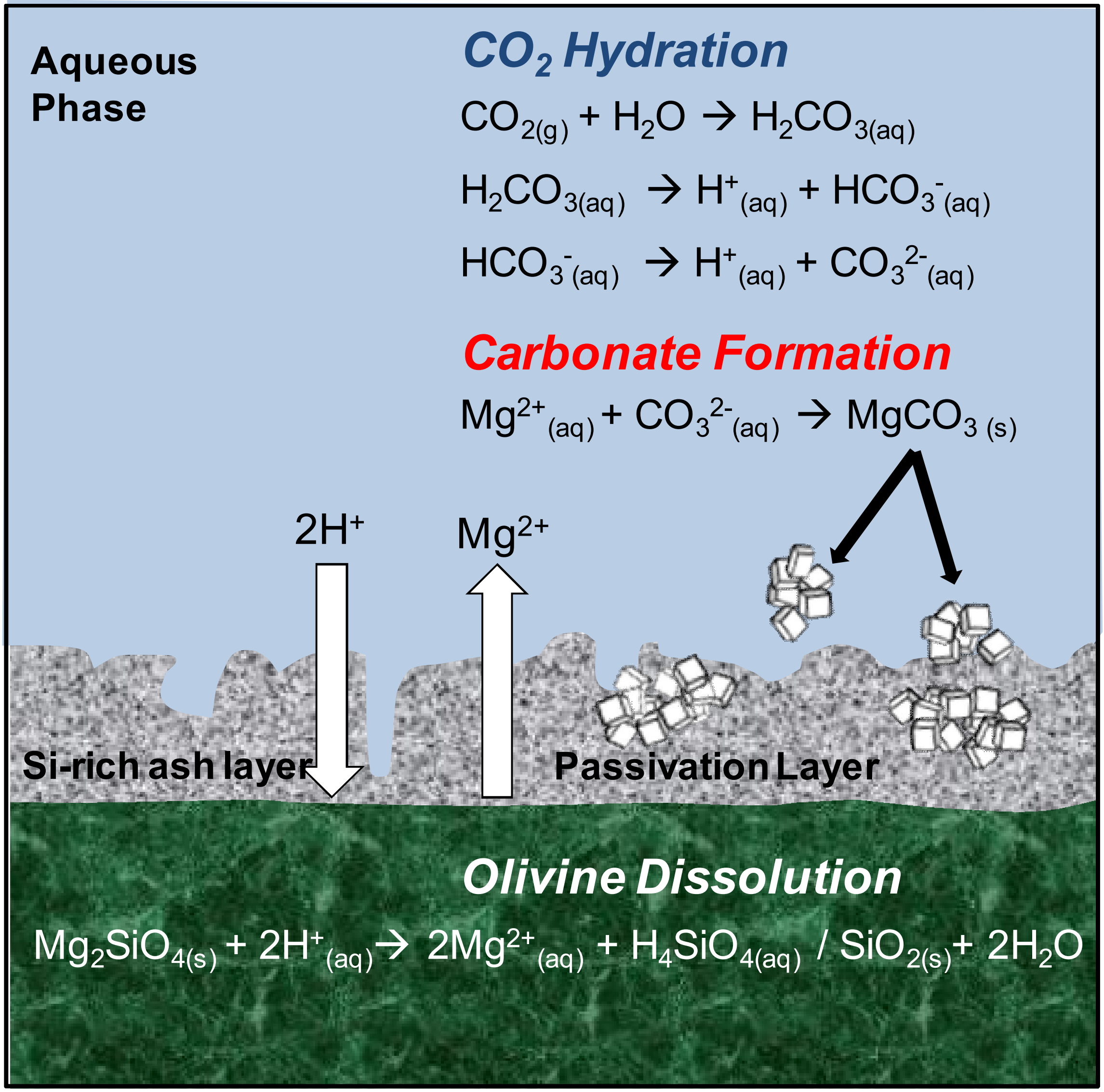
Photo by Dr. Jürg Matter at LDEO (2008)

● Basalt

● Anorthite (Labradorite)

● Magnesium-based Ultramafic Rocks (Serpentine, Olivine)

Olivine Carbonation Reaction Scheme



CO_2 Hydration

$CO_{2(g)} + H_2O \rightarrow H_2CO_{3(aq)}$

$H_2CO_{3(aq)} \rightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$

$HCO_3^-{}_{(aq)} \rightarrow H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

Carbonate Formation

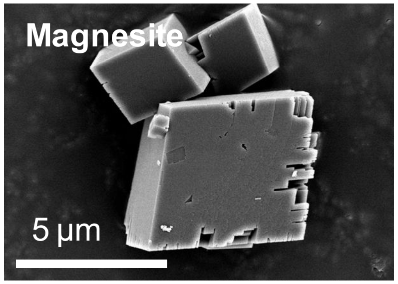
$Mg^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow MgCO_{3\,(s)}$

Olivine Dissolution

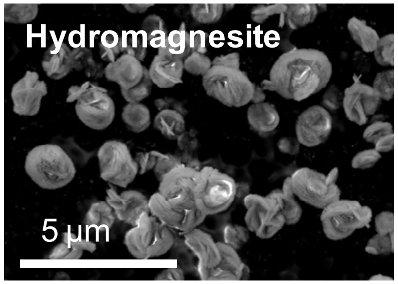
$Mg_2SiO_{4(s)} + 2H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + H_4SiO_{4(aq)}\ /\ SiO_{2(s)} + 2H_2O$

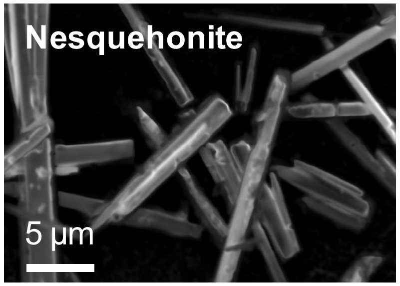
Magnesium Carbonate Phases

High temperature



Low temperature

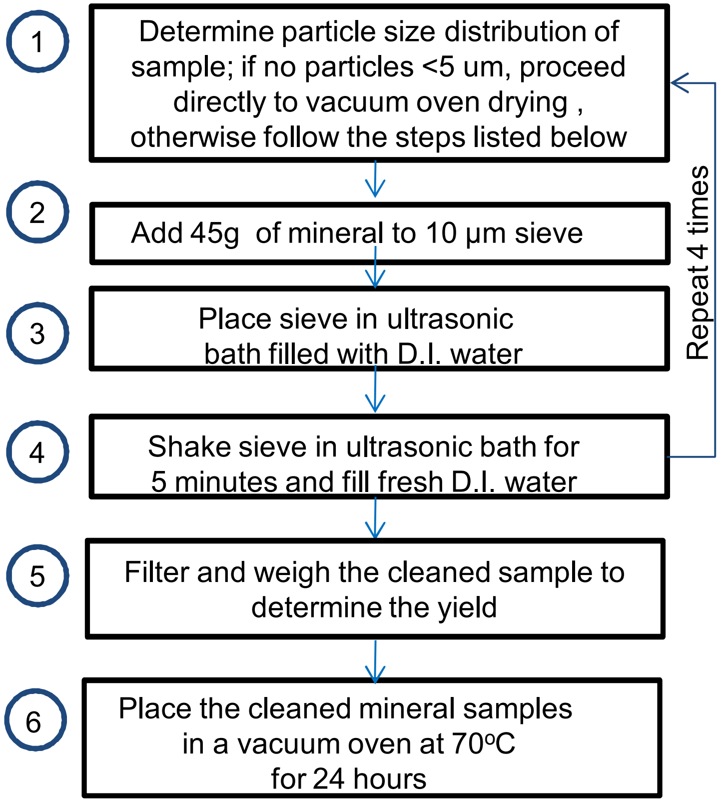




Minerals of Interest

Mineral	**MgO**	**CaO**	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	V_2O_5	LOI%	Sum %	Ni %
Olivine	**47.3**	**0.16**	**13.9**	**39.7**	**0.2**	0.01	<0.01	<0.01	< 0.01	0.15	0.78	< 0.01	-0.7	101.5	0.27
Anorthosite	**8.74**	**14.1**	**10.6**	**41.8**	**24.2**	0.59	0.03	0.04	< 0.01	0.13	0.08	< 0.01	0.12	100.4	0.02
Labradorite	**0.24**	**10.2**	**0.97**	**54.3**	**28.0**	5.05	0.59	0.14	0.04	0.01	0.10	<0.01	0.32	99.8	N/A
Basalt	**4.82**	**8.15**	**14.6**	**51.9**	**13.4**	2.91	1.09	1.74	0.32	0.21	0.10	0.06	0.27	99.6	0.04

Mineral Cleaning Protocol

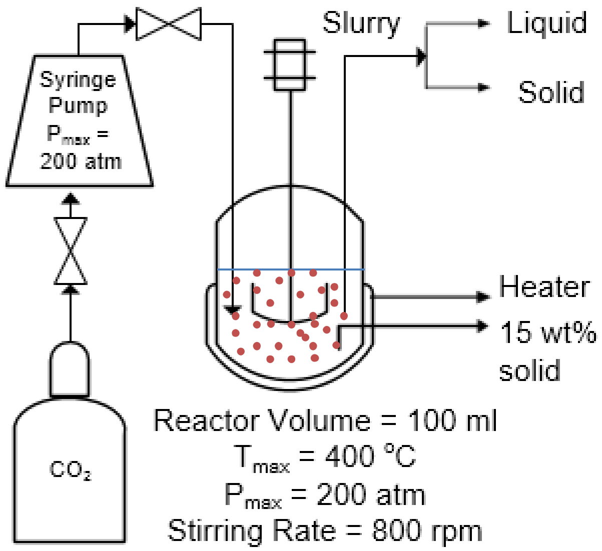


1. Determine particle size distribution of sample; if no particles <5 um, proceed directly to vacuum oven drying , otherwise follow the steps listed below
2. Add 45g of mineral to 10 μm sieve
3. Place sieve in ultrasonic bath filled with D.I. water
4. Shake sieve in ultrasonic bath for 5 minutes and fill fresh D.I. water
5. Filter and weigh the cleaned sample to determine the yield
6. Place the cleaned mineral samples in a vacuum oven at 70ºC for 24 hours

Compositions of Mixture Minerals (wt%)

	Anorthosite	**Basalt (Columbia River)**
Anorthite	63.3	20.3
Albite	2.6	24.6
Diopside	3.4	7.9
Enstatite	-	8.3
Forsterite	14.1	-
Fayalite	10.4	-

Experimental Set-up for Mineral Carbonation Studies



- Useful for simulating in-situ conditions
- Estimate changes in physical structure such as porosity, surface area etc.,
- pH changes over time
- Appropriate for determining long-term (~days) CO_2-mineral-water interactions

Post-Reaction Analysis

ICP-AES
Total Carbon Analysis
Total Inorganic Carbon Analysis
Thermogravimetric Analysis
X-Ray Diffraction
SEM-EDS
Particle Size Analysis
BET

(Wt%)	**Olivine (Mg_2SiO_4)**
MgO	47.3
CaO	0.2
Fe_2O_3	13.9
Al_2O_3	0.2
SiO_2	39.7

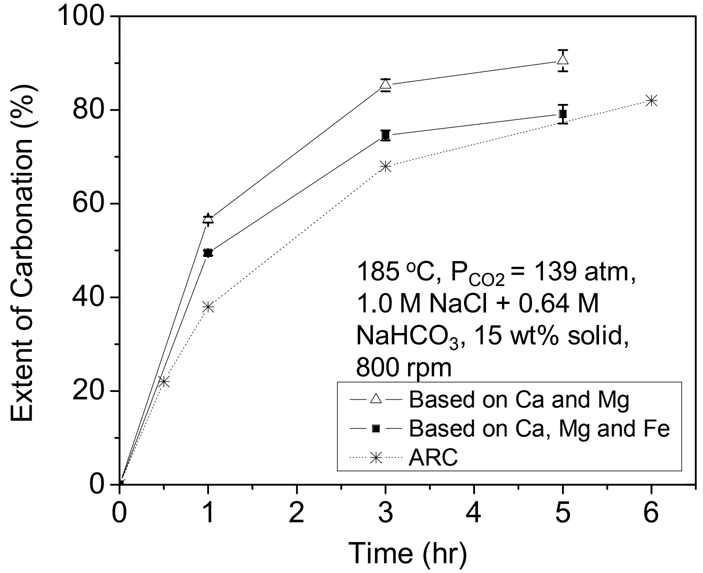
Key Questions

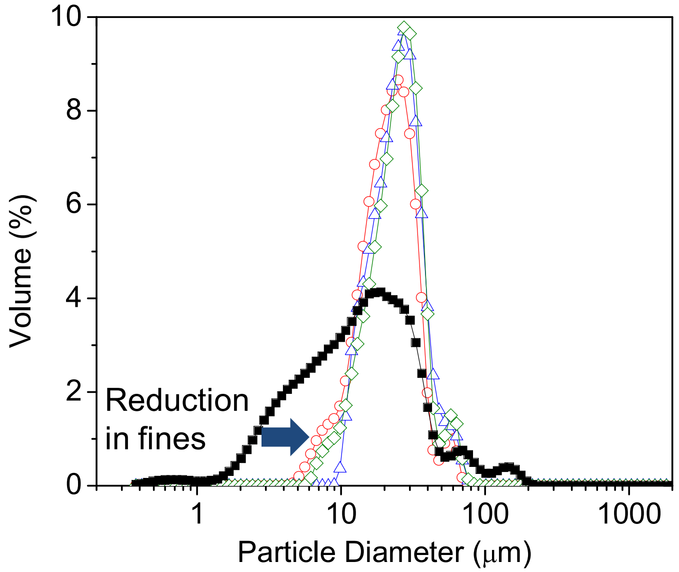
What are the rate limiting steps?

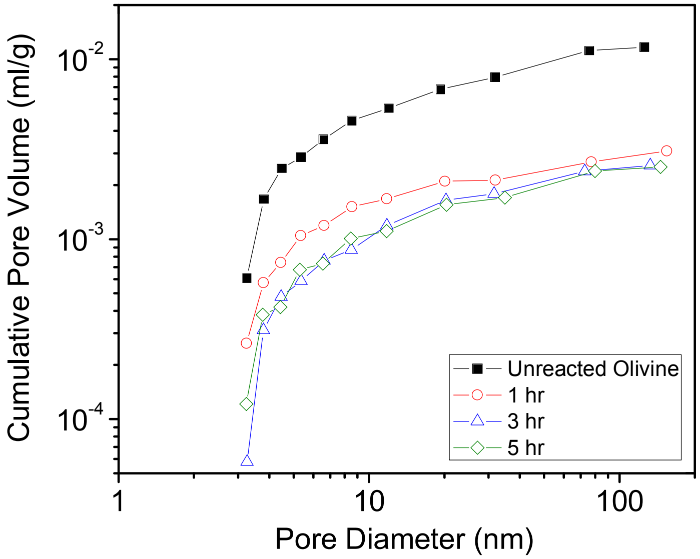
What is the role of reaction time, P_{CO2} and temperature?

What is the effect of additives such as NaCl and $NaHCO_3$ and why?
- Speculations that $NaHCO_3$ is a “catalyst”
- Evidence of $NaHCO_3$ as a buffer and carbon carrier

Effect of Reaction Time on Olivine Carbonation

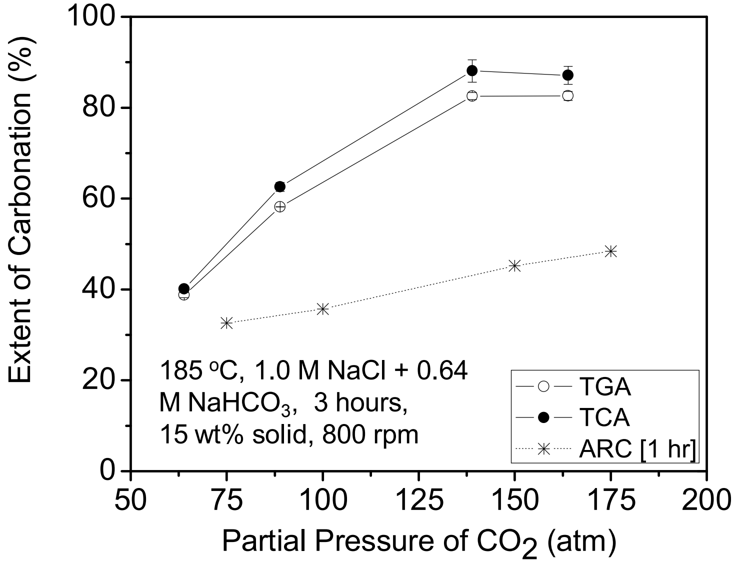


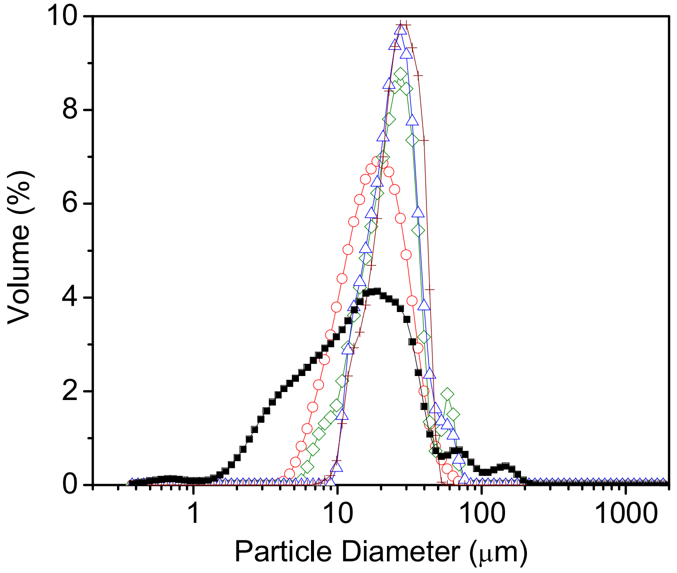


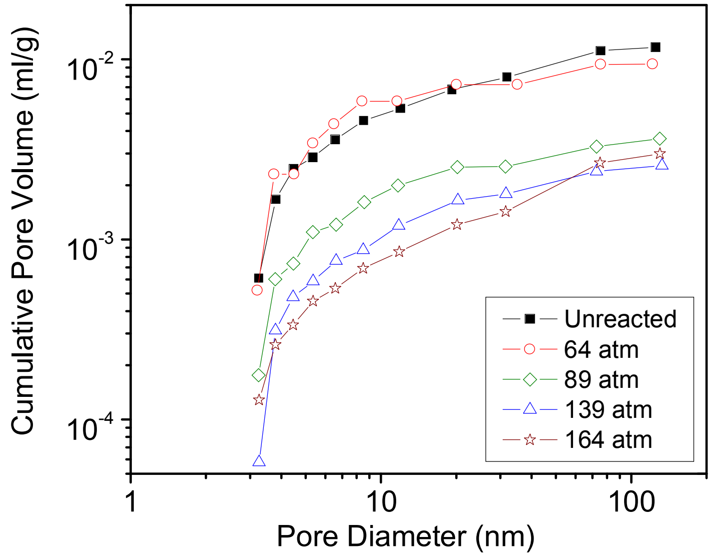


- Reaction rate increases significantly for up to 3 hours
- Significant reduction in the fine particles smaller than 10 μm and sharper distributions due to carbonation
- Order of magnitude reduction in pore volume
- Surface area reduced from 3.77 m^2/g to 1.25, 0.96 and 0.15 m^2/g after 1, 3 and 5 hr reaction times

Effect of CO_2 Partial Pressure on Olivine Carbonation





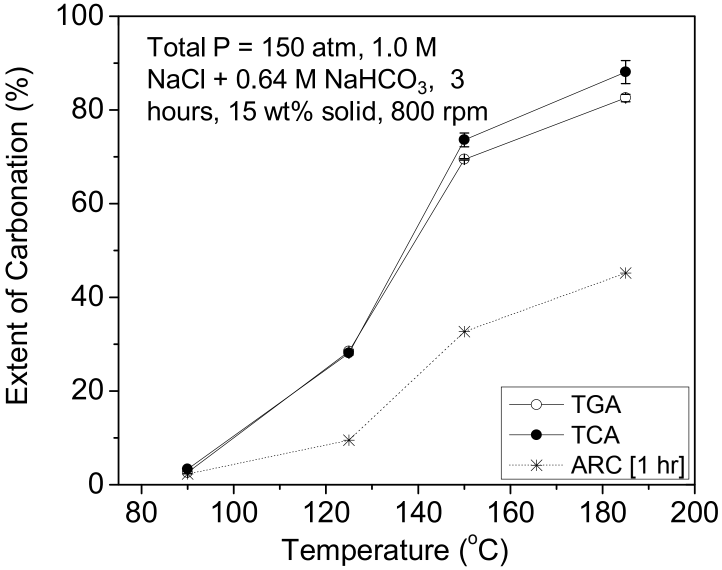


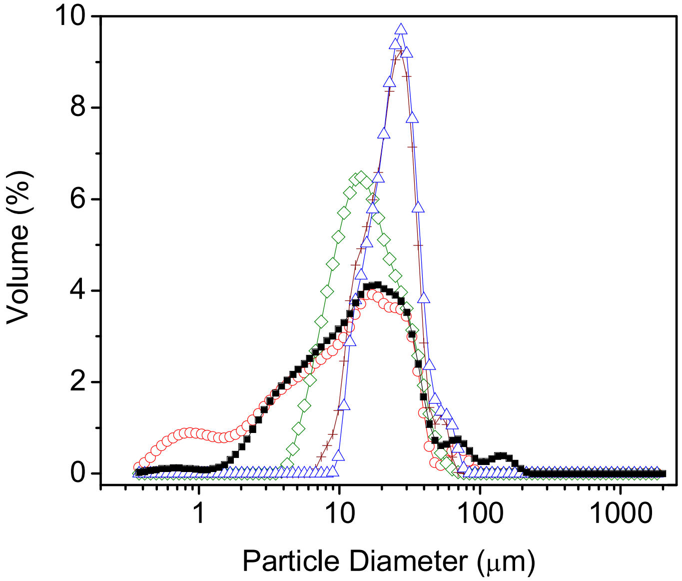
- Increasing CO_2 partial pressure enhances carbonation upto 139 atm and does not enhance carbonation beyond 139 atm

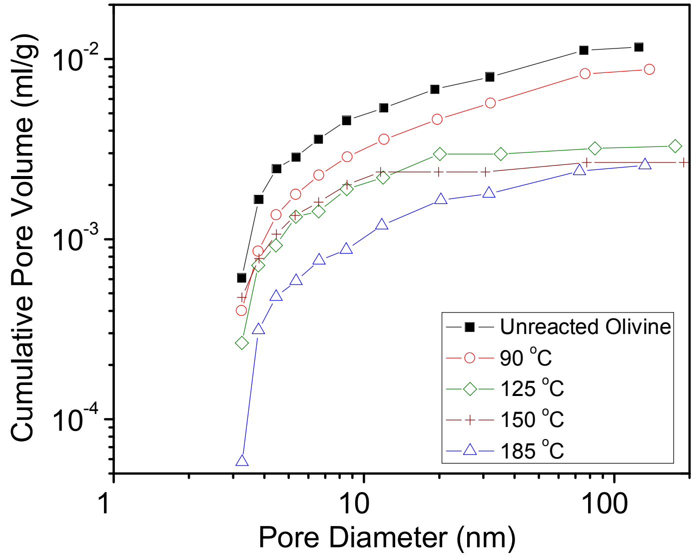
- As conversion is enhanced, particle size distribution becomes narrower and pore volume decreases progressively.

- Surface area reduced from 3.77 m^2/g to 3.20, 1.73, 0.96 and 0.80 m^2/g for PCO2 = 64, 89, 139 and 164 atm, respectively.

Effect of Temperature on Olivine Carbonation

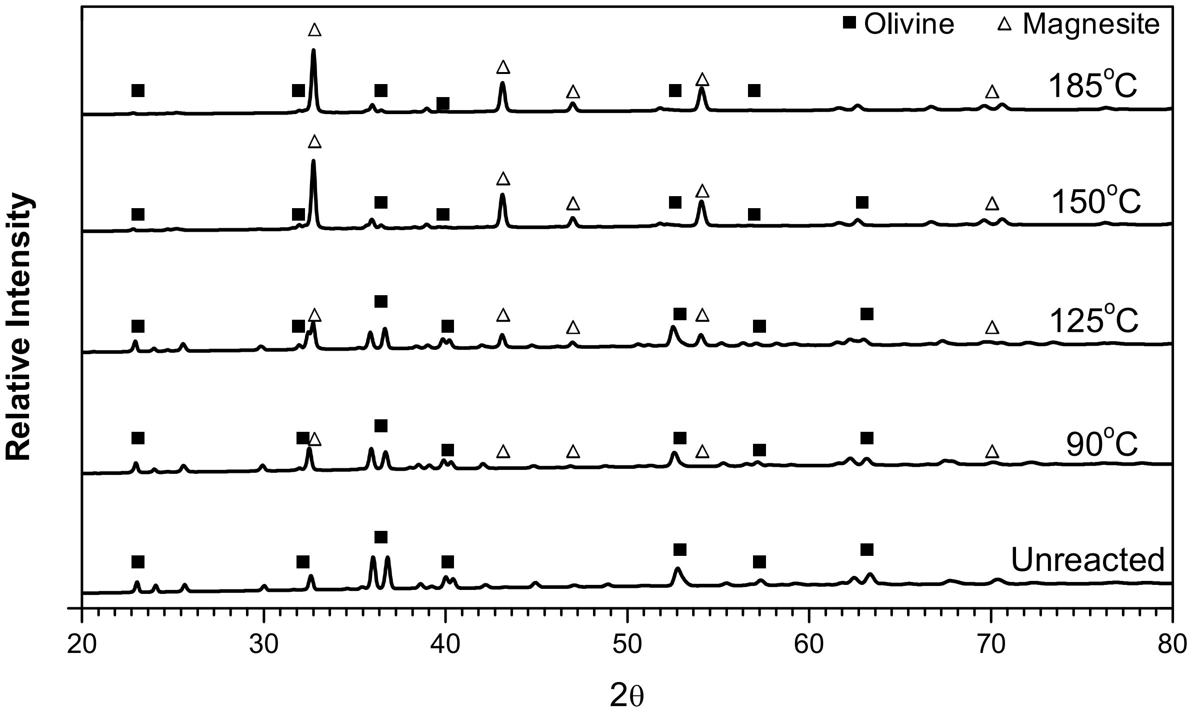


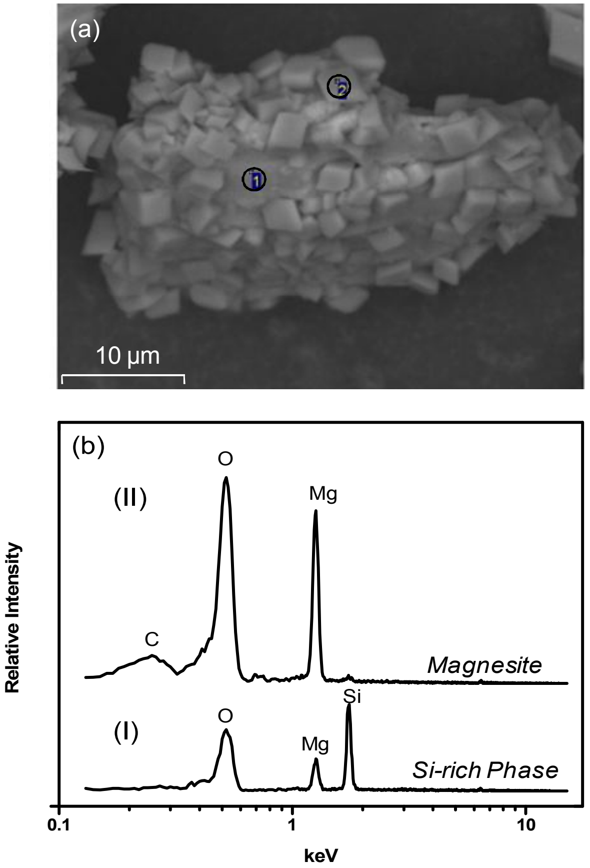




- Increasing temperature enhances mineral dissolution and carbonation kinetics
- As conversion is enhanced, particle size distribution becomes narrower and pore volume decreases progressively.
- Surface area reduced from 3.77 m^2/g to 2.01, 1.10, 1.07 and 0.96 m^2/g for 90, 125, 150 and 185 ^oC, respectively.

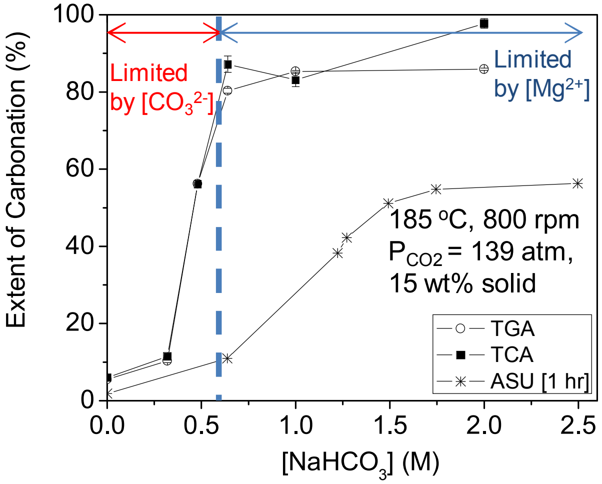
Phase Transformation of Olivine

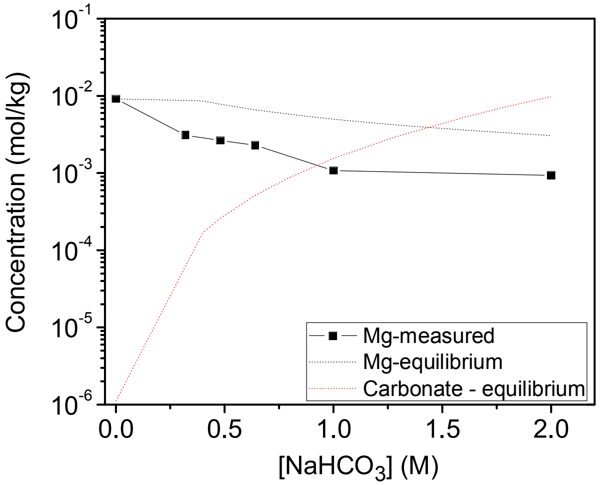




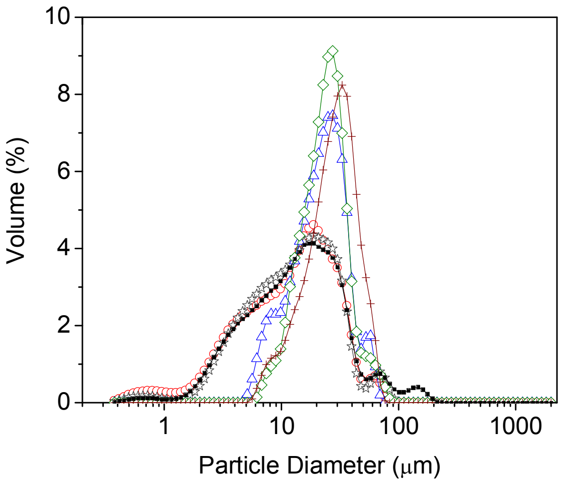
- Dominant formation of magnesite ($MgCO_3$)
- Hydrous $MgCO_3$ phases were not formed in the range of 90-185 °C

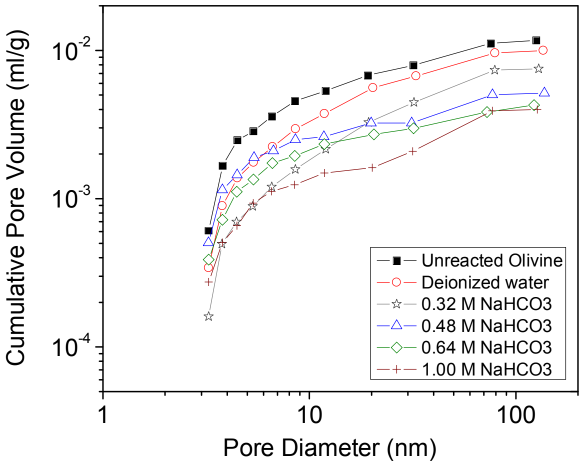
Effect of $NaHCO_3$ on Olivine Carbonation





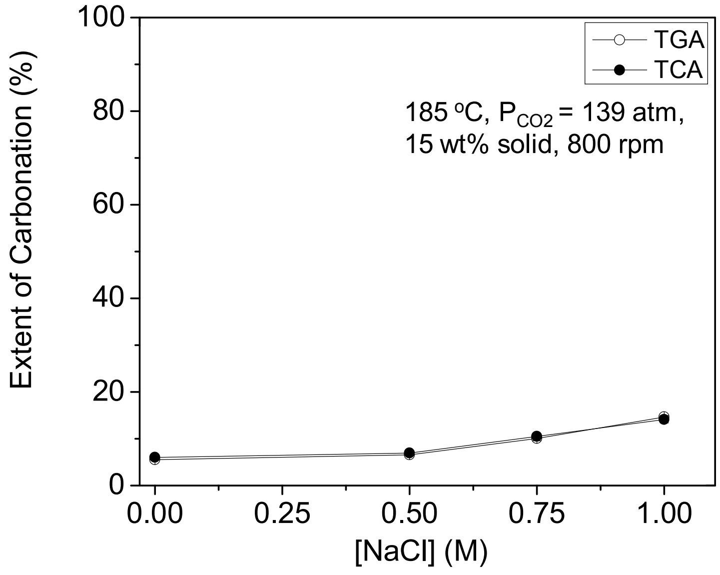
- Role of $NaHCO_3$ is that of a pH buffer and a carbon carrier.
- $NaHCO_3$ facilitates shifts in pH to favor mineral carbonation

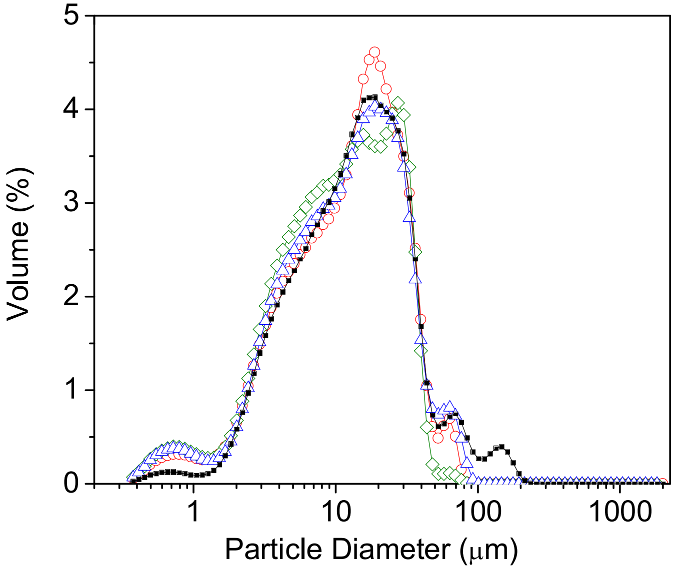


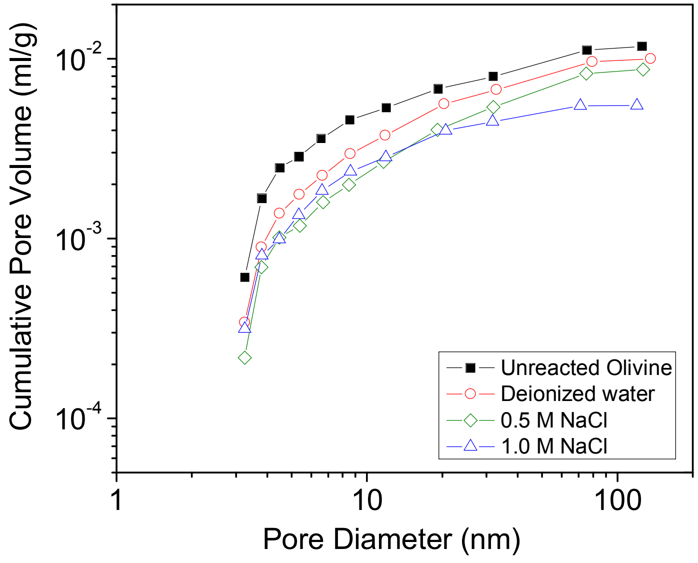


- Surface area decreased from 3.77, 1.63, 1.51, 1.20, 1.15, 1.15 m2/g in DI Water, 0.32 M, 0.48 M, 0.64 M, 1.0 M and 2.0 M $NaHCO_3$
- Progressive decrease in pore volume and increase in particle size with increasing carbonation

Effect of NaCl on Olivine Carbonation

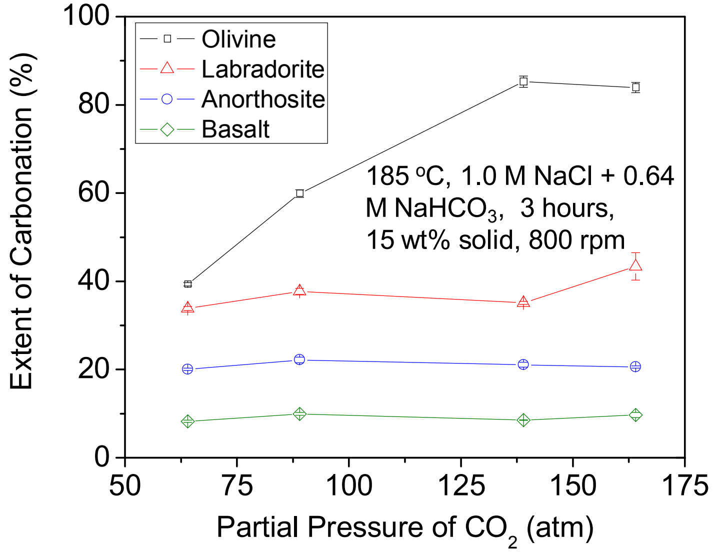




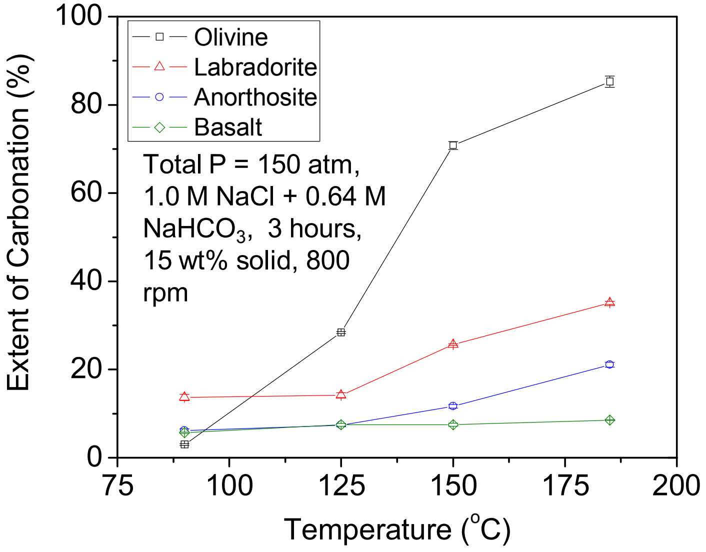


- Significant precipitation of iron oxide in the absence of $NaHCO_3$ which may have limited reactivity of mineral
- Inadequate pH buffering and availability of carbonate ions which limits extent of olivine carbonation

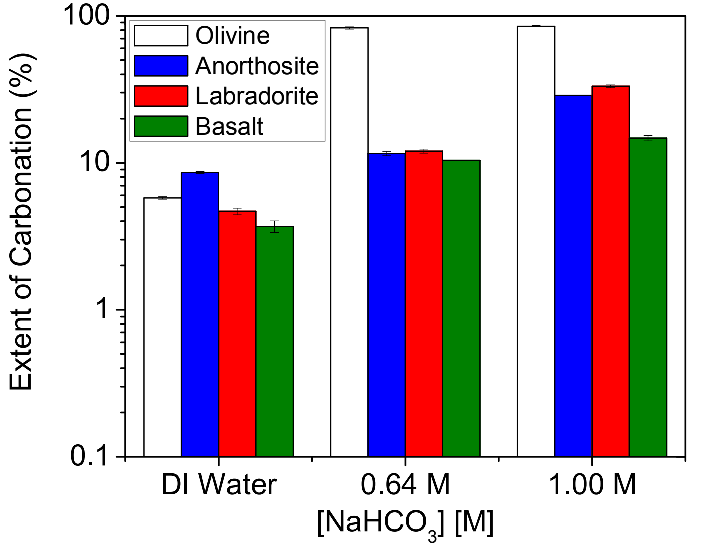
Effect of CO_2 Partial Pressure, Temperature and Additives on Various Minerals

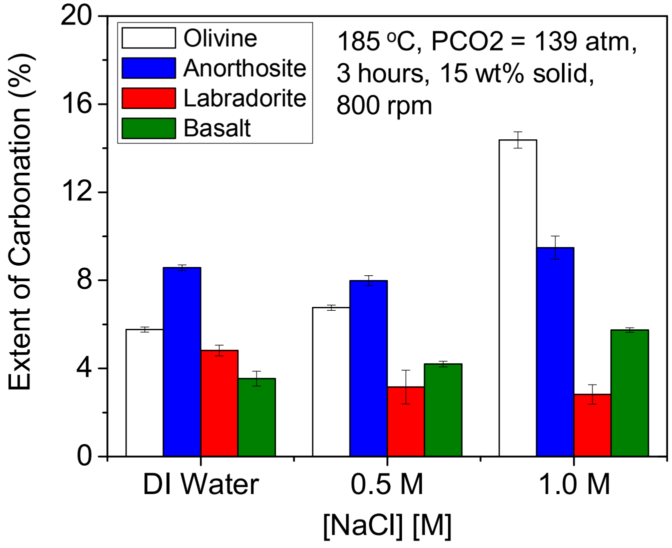


185 °C, 1.0 M NaCl + 0.64 M $NaHCO_3$, 3 hours, 15 wt% solid, 800 rpm



Total P = 150 atm, 1.0 M NaCl + 0.64 M $NaHCO_3$, 3 hours, 15 wt% solid, 800 rpm

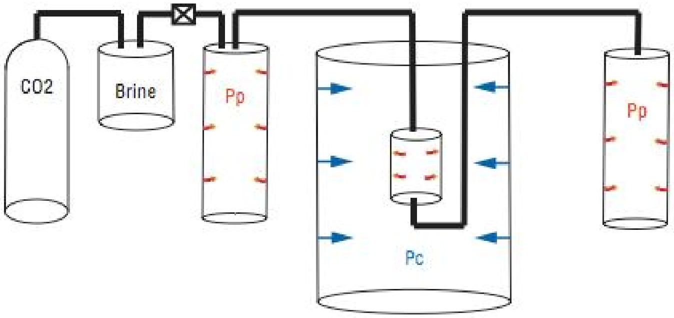




185 °C, PCO2 = 139 atm, 3 hours, 15 wt% solid, 800 rpm

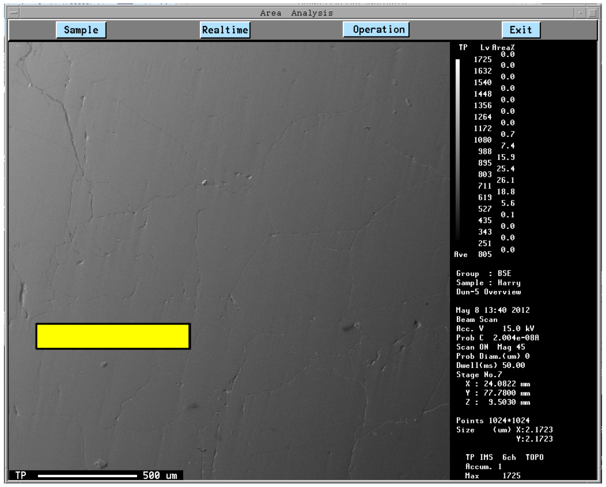
Reactive Cracking

Objective: Assess the effect of high CO_2 fluids on the behavior of ultramafic rocks such as hydrostatic compaction, constant strain rate and constant displacement creep experiments on thermally cracked dunite saturated with CO_2-saturated brines

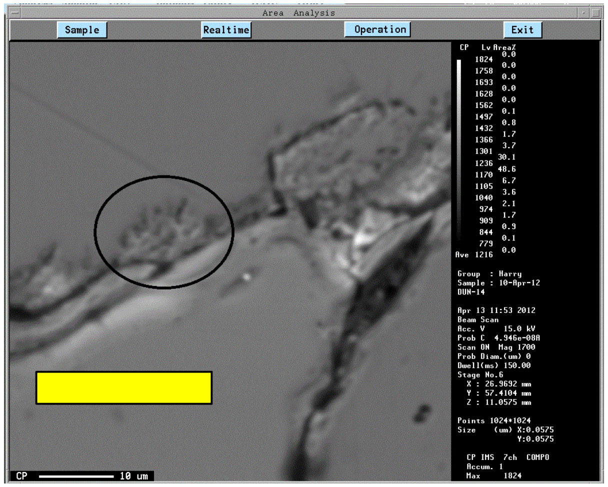


- Autolab 1500 triaxial deformation apparatus from New England Research (NER)
- Retrofitted fluid mixing system
- Independent T, P_{CO2} control
- 15 MPa confining pressure
- 10 MPa pore pressure
- 150ºC Temperature
- Thermally cracked dunite with ~ 1 mm grain size

Deformation of Rocks due to Reactive Cracking

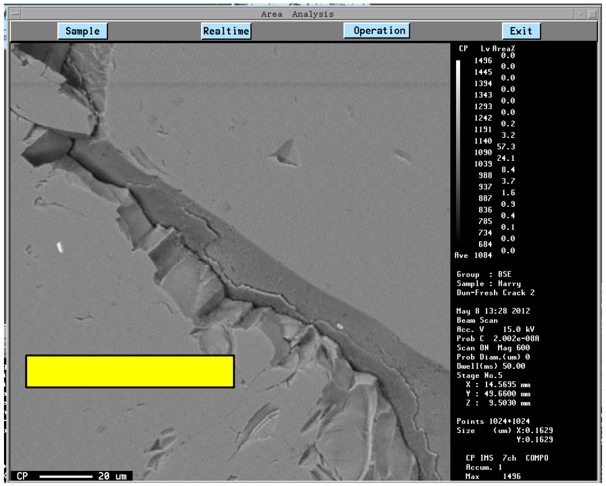


```
TP   Lv Area%
          0.0
   1725   0.0
   1632   0.0
   1540   0.0
   1448   0.0
   1356   0.0
   1264   0.0
   1172   0.7
   1080   7.4
    988  15.9
    895  25.4
    803  26.1
    711  18.8
    619   5.6
    527   0.1
    435   0.0
    343   0.0
    251   0.0
Ave  805

Group  : BSE
Sample : Harry
Dun-5 Overview

May 8 13:40 2012
Beam Scan
Acc. V    15.0 kV
Prob C  2.004e-08A
Scan ON  Mag 45
Prob Diam.(um) 0
Dwell(ms) 50.00
Stage No.7
  X : 24.0822 mm
  Y : 77.7800 mm
  Z :  9.5030 mm

Points 1024*1024
Size    (um) X:2.1723
             Y:2.1723

  TP IMS  6ch  TOPO
  Accum. 1
  Max     1725
```



```
CP   Lv Area%
          0.0
   1824   0.0
   1758   0.0
   1693   0.0
   1628   0.0
   1562   0.1
   1497   0.8
   1432   1.7
   1366   3.7
   1301  30.1
   1236  48.6
   1170   6.7
   1105   3.6
   1040   2.1
    974   1.7
    909   0.9
    844   0.1
    779   0.0
Ave 1216

Group  : Harry
Sample : 10-Apr-12
DUN-14

Apr 13 11:53 2012
Beam Scan
Acc. V    15.0 kV
Prob C  4.946e-08A
Scan ON  Mag 1700
Prob Diam.(um) 0
Dwell(ms) 150.00
Stage No.6
  X : 26.9692 mm
  Y : 57.4104 mm
  Z : 11.0575 mm

Points 1024*1024
Size    (um) X:0.0575
             Y:0.0575

  CP IMS  7ch  COMPO
  Accum. 1
  Max     1824
```

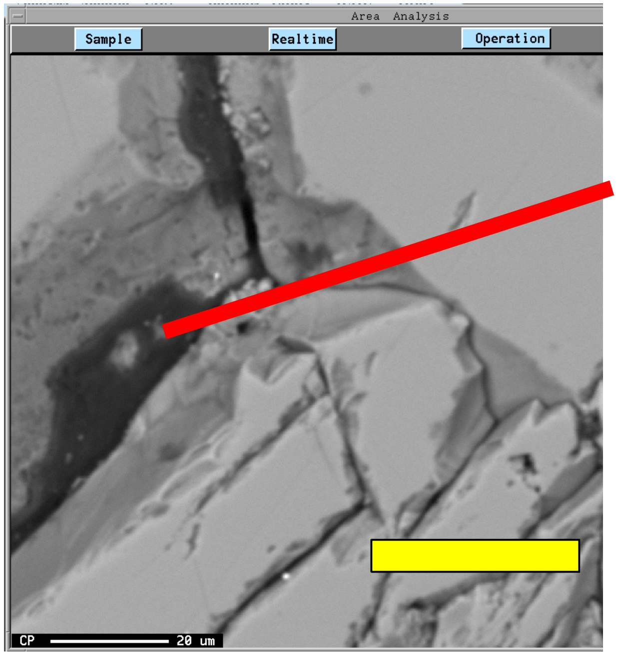
- Deformed with reactive brine
- Pitting, signs of dissolution of olivine



```
CP   Lv Area%
          0.0
   1496   0.0
   1445   0.0
   1394   0.0
   1343   0.0
   1293   0.0
   1242   0.2
   1191   3.2
   1140  57.3
   1090  24.1
   1039   8.4
    988   3.7
    937   1.6
    887   0.9
    836   0.4
    785   0.1
    734   0.0
    684   0.0
Ave 1084

Group  : BSE
Sample : Harry
Dun-Fresh Crack 2

May 8 13:28 2012
Beam Scan
Acc. V    15.0 kV
Prob C  2.002e-08A
Scan ON  Mag 600
Prob Diam.(um) 0
Dwell(ms) 50.00
Stage No.5
  X : 14.5695 mm
  Y : 49.6600 mm
  Z :  9.5030 mm

Points 1024*1024
Size    (um) X:0.1629
             Y:0.1629

  CP IMS  7ch  COMPO
  Accum. 1
  Max     1496
```

smooth, uniform crack surfaces in thermally cracked dunite

supported by DOE DE-FE0002386 & C11E10947



Accomplishments to Date

- Quantified extents of carbonation of the olivine and anorthite as a function of temperature, partial pressure of CO_2 and in the presence of various additives

- Demonstrated significant changes in pore structure, morphology and particle size occur after carbonation and dissolution

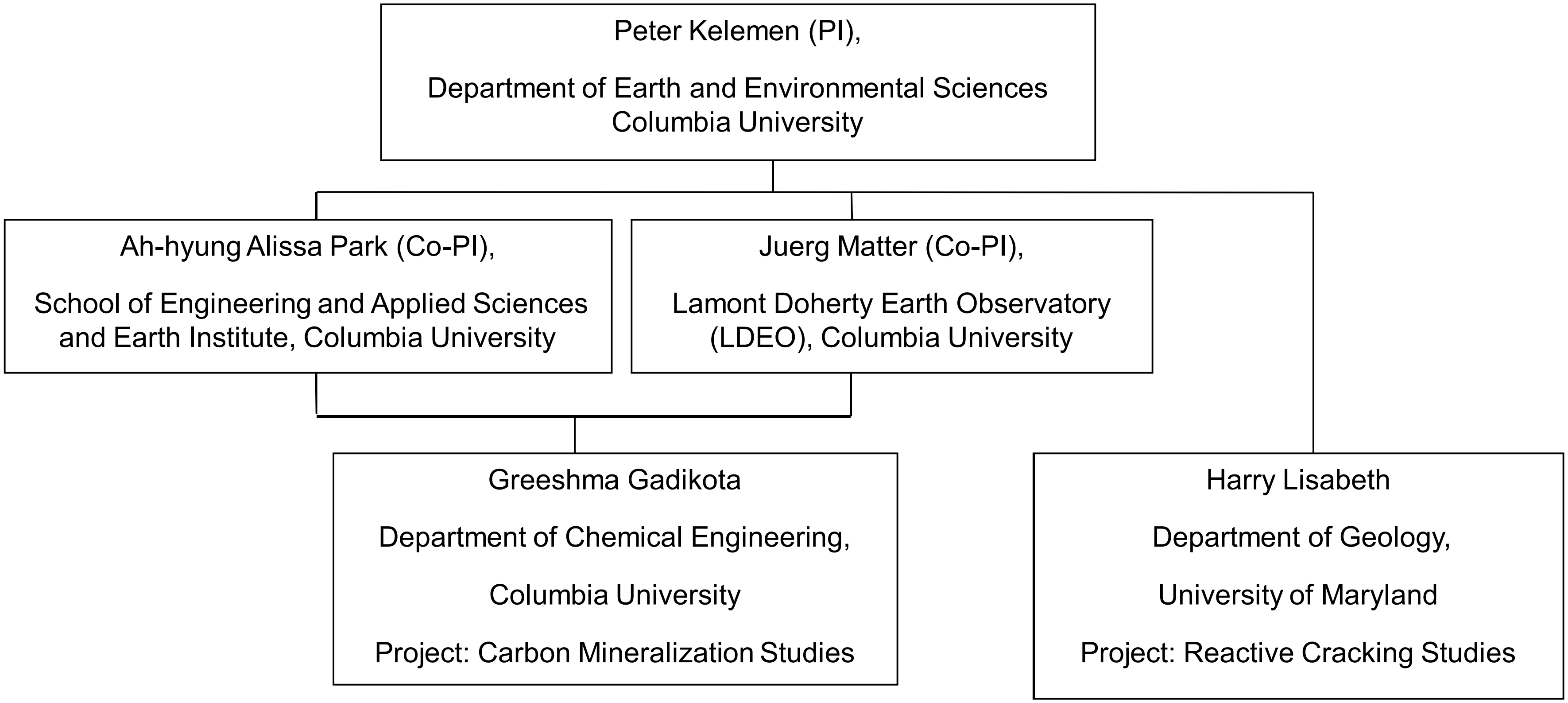
- Initial mineral dissolution rates are substantially higher than longer-term rates with preferential leaching of Mg which has implications for long-term storage of CO_2 in geologic formations

- Determined that reactive brines cause samples to deform more rapidly due to olivine dissolution

Summary

- Higher temperatures and presence of additives such as NaCl and $NaHCO_3$ have a significant impact on enhancing mineral carbonation
- Significant reduction in pore size and surface area after carbonation is evident
- In terms of reactivity with CO_2: olivine > labradorite> anorthosite > basalt
- Reactive brines cause samples to deform more rapidly due to olivine dissolution
- Rapid deformation is apparently due to olivine dissolution, reducing solid-solid contact area along fractures
- Permeability drops due to mechanical compaction are delayed; there is a sudden loss of connectivity, but not of porosity

Organization Chart



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Project: Carbon Mineralization Studies

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Project: Reactive Cracking Studies

Gantt Chart

Tasks	Year I				Year II				Year III				Year 4 (NCE)			
	Qt1	Qt2	Qt3	Qt4	Qt1	Qt2	Qt3	Qt4	Qt1	Qt2	Qt3	Qt4	Qt1	Qt2	Qt3	Qt4
Task 1.0 Project Management, Planning and Reporting	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Task 2.0 Laboratory Experiments on Carbonation Kinetics of Peridotite and Basalt																
Subtask 2.1 Selection of rocks to be studied	■	■														
Subtask 2.2. Determination of mineralization with varying pressure		■	■	■	■											
Subtask 2.3 Determination of mineral rates under varying temperature						■	■	■	■	■	■	■	■	■	■	■
Subtask 2.4 Analysis of carbonated samples				■	■	■	■	■	■	■	■	■	■	■	■	■
Task 3.0 Laboratory Study of Catalytic Effects on Carbonation Kinetics of Peridotite and Basalt																
Subtask 3.1 Selection of minerals and basaltic glass to be studied	■															
Subtask 3.2 Mineralization as a function of varied mineral composition		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Subtask 3.3 Mineralization as a function of varied pressure		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Subtask 3.4 Varied temperature and/or combined variables						■	■	■	■	■	■	■	■	■	■	■
Subtask 3.5 Analysis of carbonated samples				■	■	■	■	■	■	■	■	■	■	■	■	■
Task 4.0 Laboratory Testing of "Reactive Cracking" Hypothesis																
3. Subtask 4.1 Initial experiments	■	■	■	■												
Subtask 4.2 Experiments with varying fluid pressure					■	■	■	■								
Subtask 4.3 Experiments with deviatoric confining pressure							■	■	■	■	■					
Subtask 4.4 Analysis of carbonated samples				■	■	■	■	■	■	■	■					

Bibliography

Journal, multiple authors:

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- Kelemen, P.B. and G. Hirth, Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation, Earth Planet. Sci. Lett 345–348, 81–89 2012
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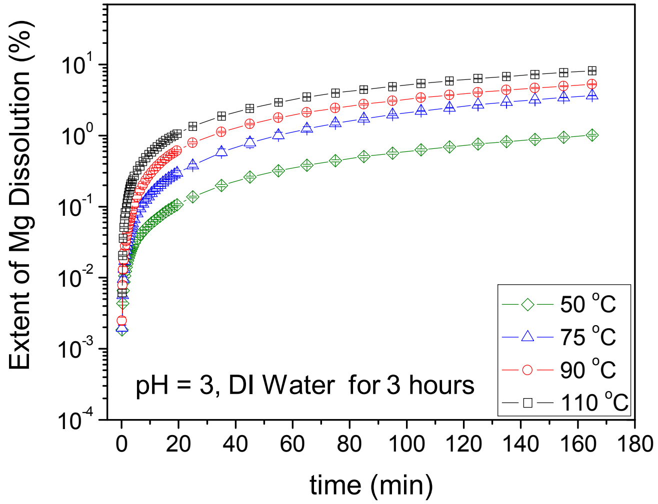
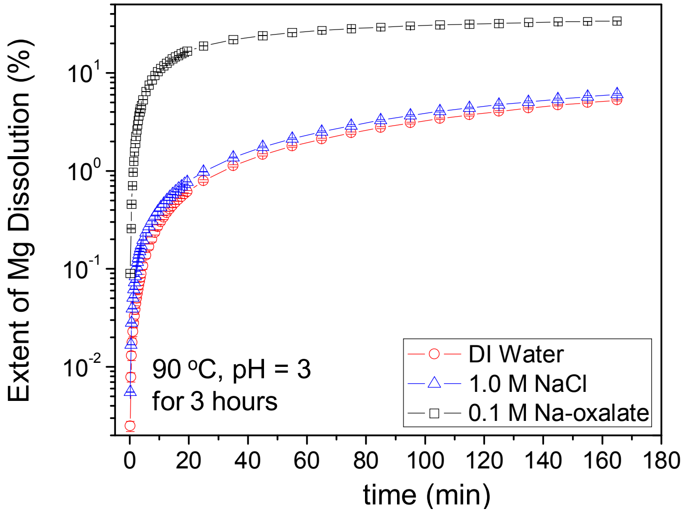
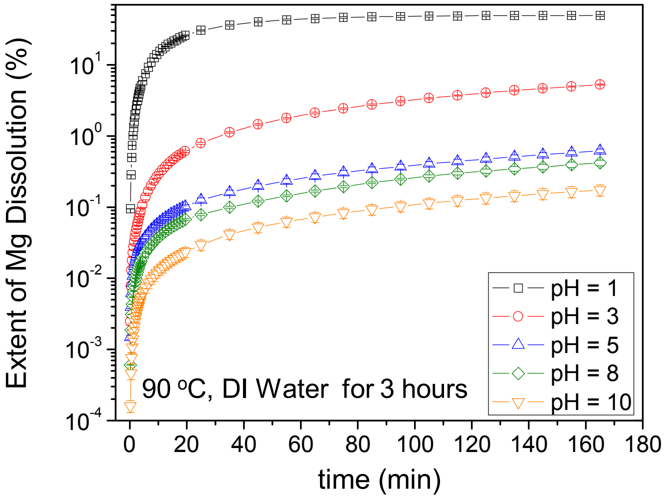
- Paukert, A.P., J.M. Matter, P.B. Kelemen, E.L. Shock and J.R. Havig, 2012, Reaction path modeling of enhanced in situ CO2 mineralization for carbon sequestration in the peridotite of the Samail Ophiolite, Sultanate of Oman: Chem. Geol., in press 2012
- Streit, E., P.B. Kelemen, and J. Eiler, Coexisting serpentine and quartz from carbonate-bearing serpentinized peridotite in the Samail Ophiolite, Oman, Contrib. Mineral. Petrol., online, DOI 10.1007/s00410-012-0775-z, 2012, print publication in press.

Effect of Temperature, pH and Chemical Additives on Olivine Dissolution Behavior







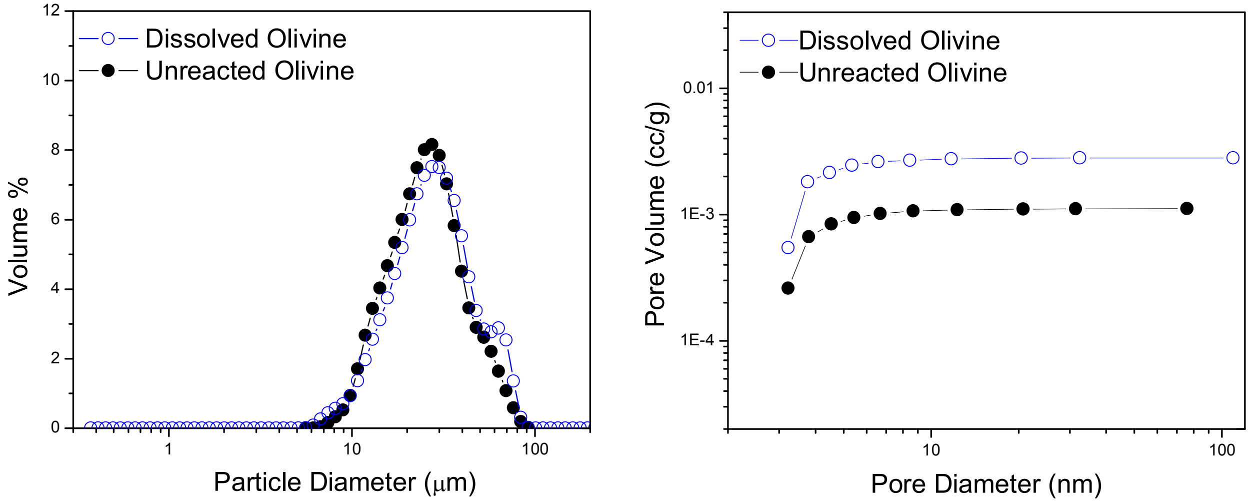
- High conversions achieved in the first 20 min after which the reaction rates decrease

- Initial surface reaction controlled mechanism and then diffusion across passivation layer dominates dissolution

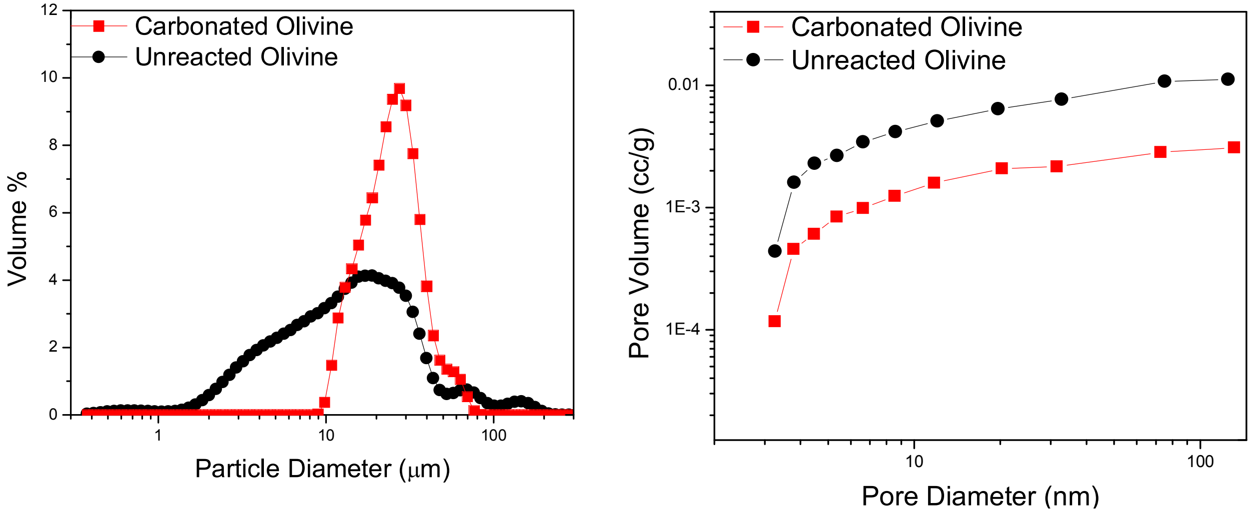
- Increasing temperature, decreasing pH and addition of chelating agents such as Na-oxalate favor dissolution

Changes in Pore Volume and Particle Size Due to Mineral Dissolution and Carbonation

Olivine Dissolution



Olivine Dissolution + Carbonation



- Particle size unchanged due to dissolution
- Pore volume increases with dissolution
- Magnesite crystal growth increases the particle size
- Fine particles < 10 μm react much faster to form carbonates
- Pore volume is considerably reduced after carbonation due to the formation of carbonate crystals in the pores
- Changes in pore volume have implications for CO_2 storage in geologic reservoirs