

Integrated Experimental and Modeling Studies of
Mineral Carbonation as a Mechanism for
Permanent Carbon Sequestration in
Mafic/Ultramafic Rocks
DE-FE0004375

Zhengrong Wang
Yale University



U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and
Infrastructure for CCS
August 20-22, 2013



Organizations

- Yale University: Jay Ague, David Bercovici, Edward Bolton, Shun-ichiro Karato, Michael Oristaglio, and Zhengrong Wang
- University of Hawaii: Kevin Johnson, Eric Hellebrand
- University of Maryland: Wen-lu Zhu
- Collaborators:
 - PNNL: Pete McGrail and Herbert Schaef



Presentation Outline

- Project Overview
- Technical Status & Accomplishments
- Key Findings
- Summary
- Accomplishment and future directions
- Appendix



Benefit to the Program

- Program goal being addressed
 - Develop technologies that will support industries' ability to predict CO₂ storage capacity in geologic formations to within ± 30 percent.
- Benefits statement
 - This research project is developing new methodology, integrating both geochemical and geomechanical experiments with reactive transport modeling, for making rigorous estimates of the permanent carbon sequestration potential in mafic and ultramafic rocks subjected to ***in situ* mineral carbonation**.



Project Overview: Goals and Objectives

- Determine, through geochemical experiments, reaction rates of the key mineral carbonation reactions in the system,
 $[\text{mafic rocks} + \text{H}_2\text{O} + \text{CO}_2] \rightarrow [\text{carbonate rocks} + \text{byproducts}]$,
by studying the influence of pressure, temperature, ionic activity, surface area, pH and extent of reaction.
- Determine, through geomechanical experiments, how pore space of basalts and other mafic/ultramafic rocks evolves during carbonation reactions, especially in the competition between cracking and pore constriction and collapse.
- Develop a calibrated numerical simulation model of *in situ* mineral carbonation that can be used to design field experiments by predicting how lab experiments scale up.



Project Overview: Success Criteria

Geochemical experiments

Experimental results for reaction products and rates repeatable to $\pm 10\%$ with consistent P/T trends

Simulation code reproduces reaction products and rates from subset of laboratory experiments with maximum error of $\pm 10\%$, after adjusting input parameters. Code predicts reaction rates to $\pm 20\%$ outside range used to adjust parameters.

Geomechanical experiments

Permeability and fracture strength measurements repeatable in experiments with fluid-rock mixtures to $\pm 20\%$.

Simulation code reproduces reaction products and rates from subset of laboratory experiments with maximum error of $\pm 20\%$, after adjusting input parameters. Code initially predicts reaction rates to $\pm 30\%$ outside range used to adjust parameters. With further refinements, code predicts reaction rates to within 20%.

Scaling up simulations show convergence to within 20% with successive grid refinement and self-consistent trends.



Project Overview: Deliverables

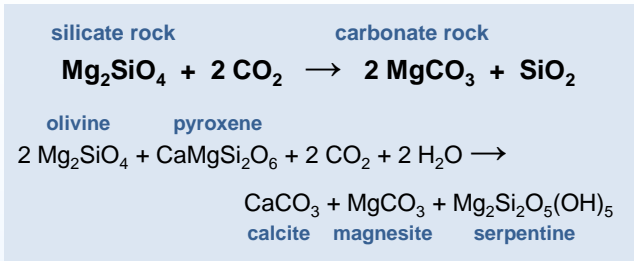
- Database Table of thermodynamic parameters and kinetic reaction rates for the main mineral carbonation reactions of mafic/ultramafic rocks
- Codes for integrated geochemical/geomechanical modeling of mineral carbonation in 0D through 3D
- Plan for Site Assessment and Characterization for a large-scale field test in a “phase-II” project (expected field site is Big Island of Hawaii)



Technical Status

- Experimental setup
- Geochemical experiments and modeling
- Geo-mechanical experiments and modeling

Experimental setup



GEOCHEMICAL Experiments on Minerals

Understand the fundamental thermodynamics & kinetics

Cold seal and flow-through experiments on mineral powders to map reaction kinetics of mineral carbonation as a function of pressure, temperature, grain size, and other control variables

Model chemical reactions and mass transport



Mineral Carbonation

GEOMECHANICAL Experiments & Modeling

Understand the feedbacks: effects of chemical reactions on rock matrix and pore space

Flow and deformation experiments with monitoring of porosity and permeability changes during mineral carbonation reactions

Model rock deformation and evolution of pore space with damage theory
Understand mechanisms of stress fracturing

SCALE UP



SCALE UP

Geochemical Experiments on Rocks

Understand rock assemblages in the lab

Cold seal and flow-through experiments on rocks

SCALE UP



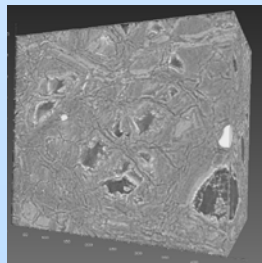
DESIGN

PHASE II FIELD STUDY

INITIAL PORE SPACE

STRESS FRACTURES
 PORE SPACE ALTERATION

REACTION KINETICS



3D micro-tomogram of carbonized dunite sample

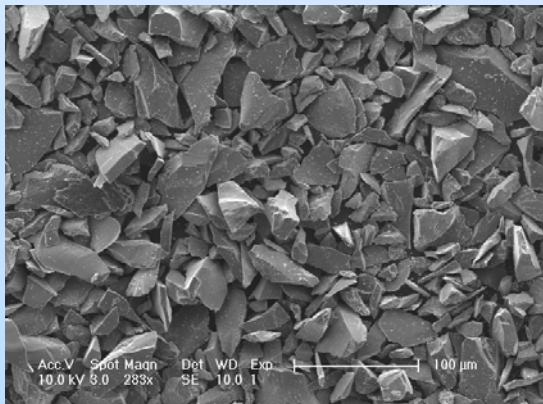
CHEMICAL
 HYDROTHERMAL
 & GEOMECHANICAL
 PROCESSES

MODELING & SIMULATION

Build an integrated simulation model for geochemical & geomechanical processes

Scaling up simulations in 2D and 3D, calibrated by experiments and field work

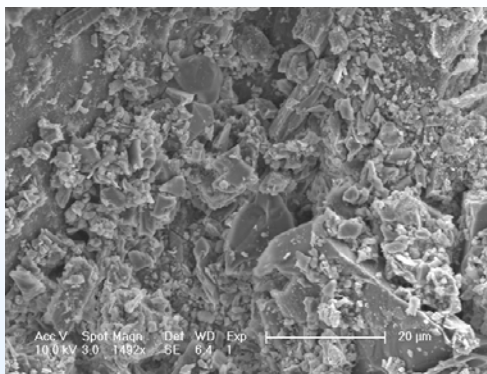
Geochemical experiments



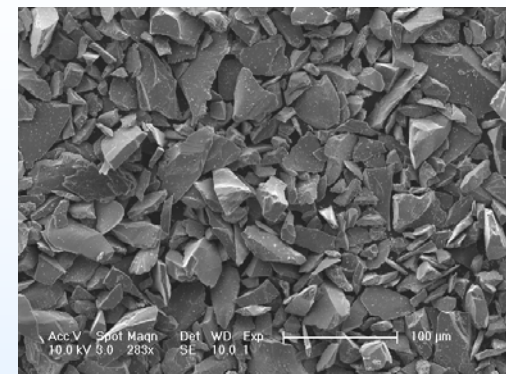
Samples



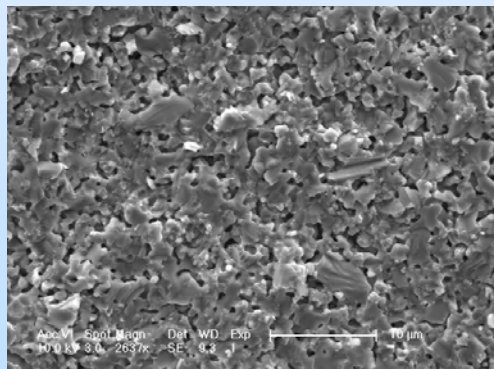
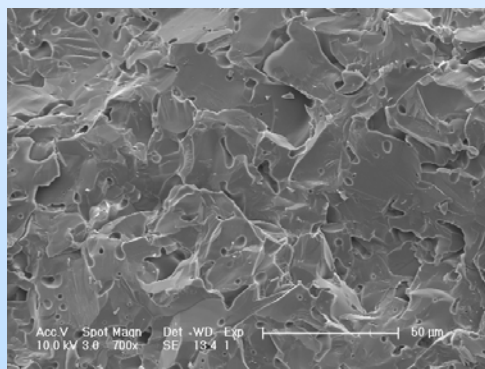
Gem-quality single crystals
(left: Olivine, Right: Garnet)



Basalt powder



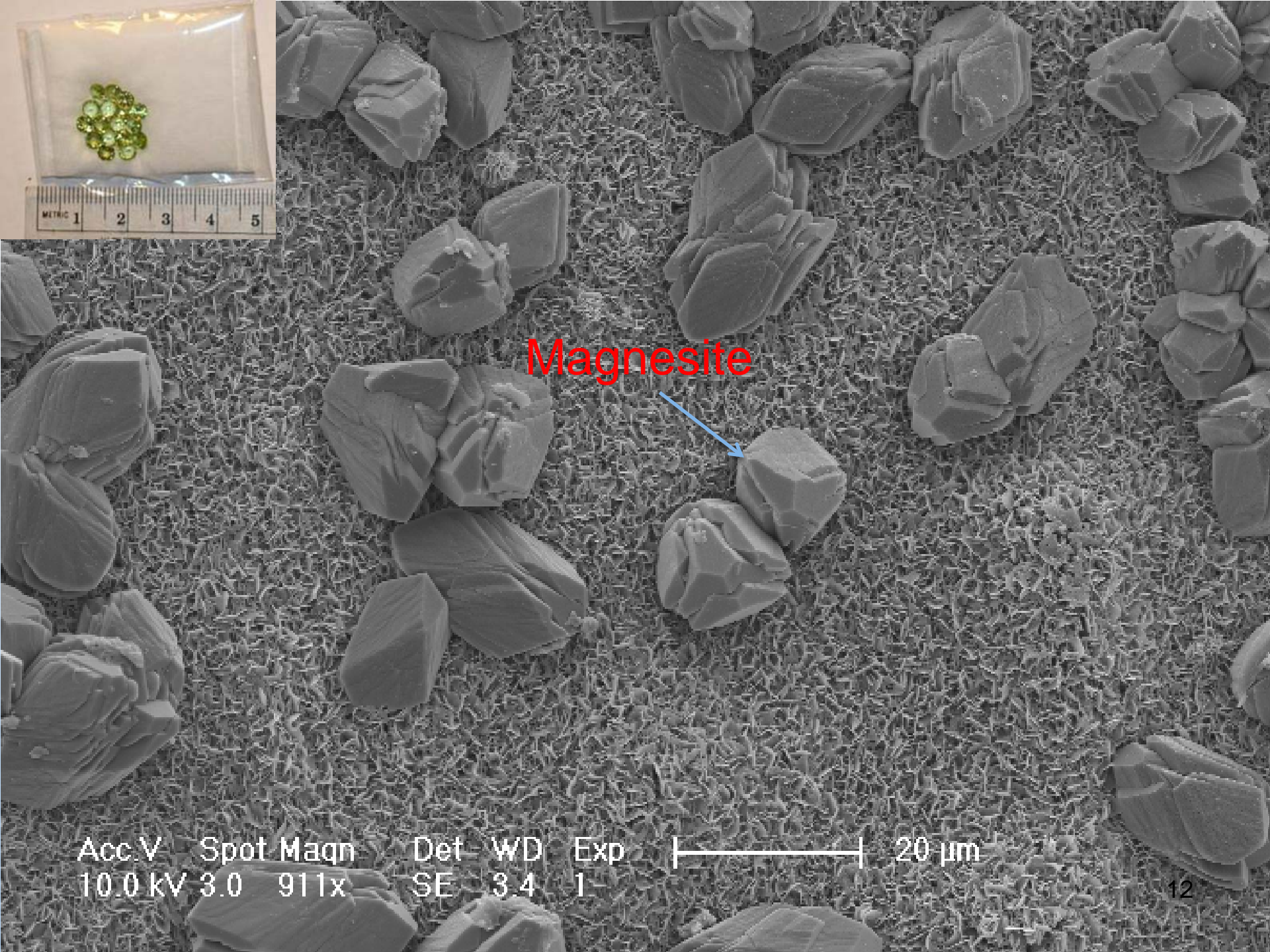
Olivine powder



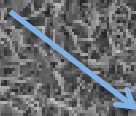
Sintered olivine and basalts



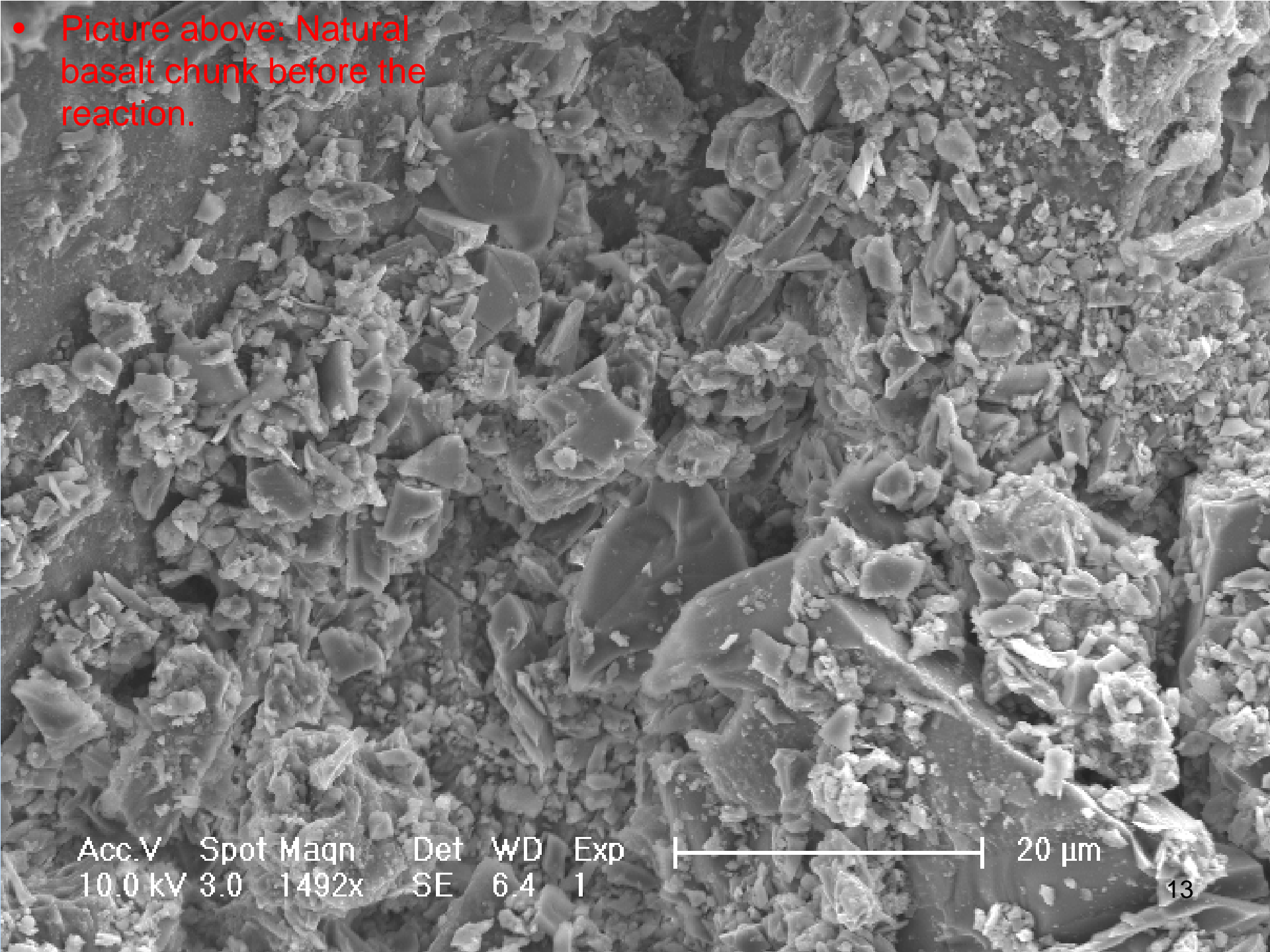
Picrite cube



Magnesite



Acc.V Spot Magn Det WD Exp |-----| 20 μm
10.0 kV 3.0 911x SE 3.4 1

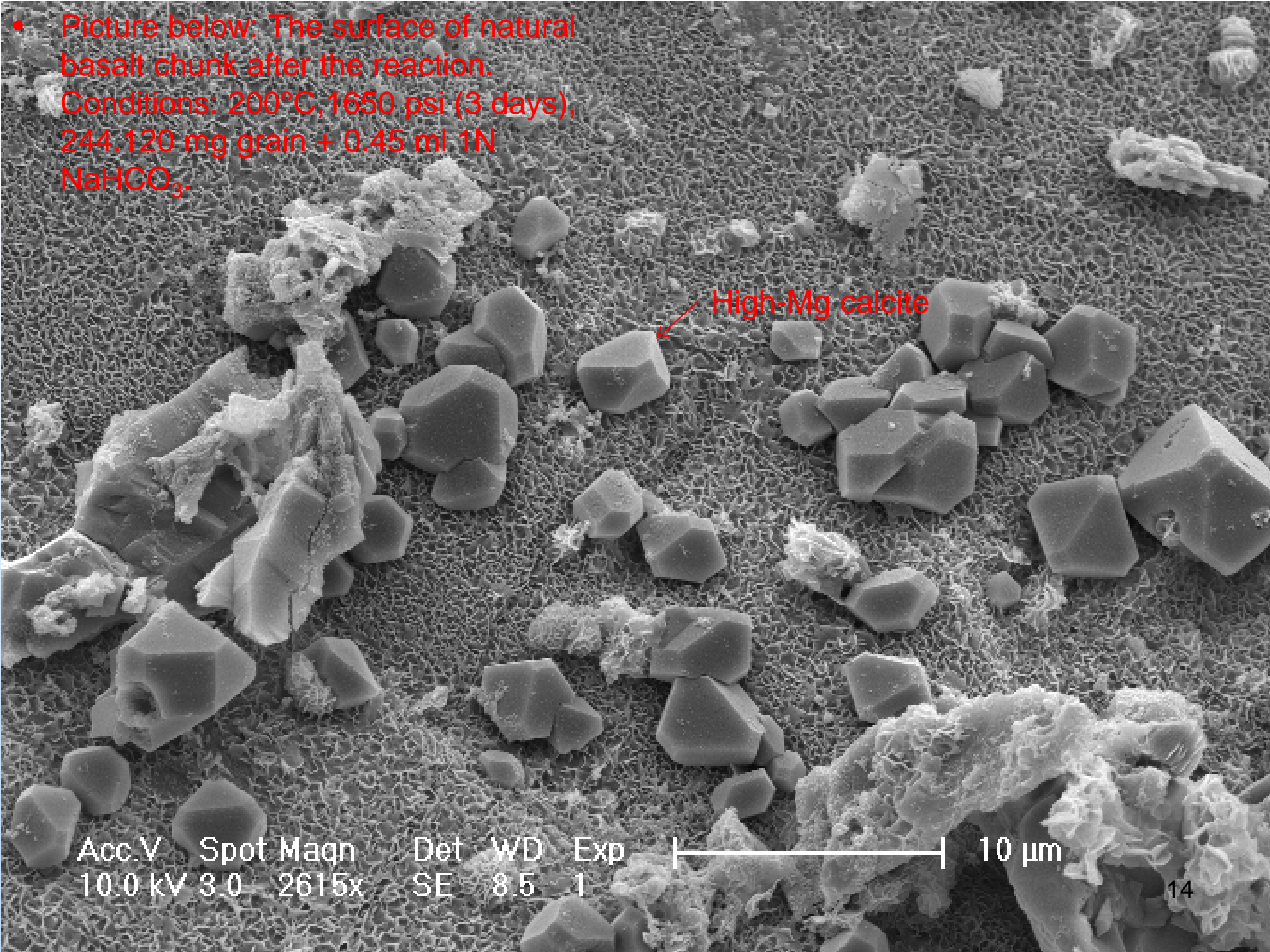


- Picture above: Natural basalt chunk before the reaction.

Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 1492x SE 6.4 1

20 μ m

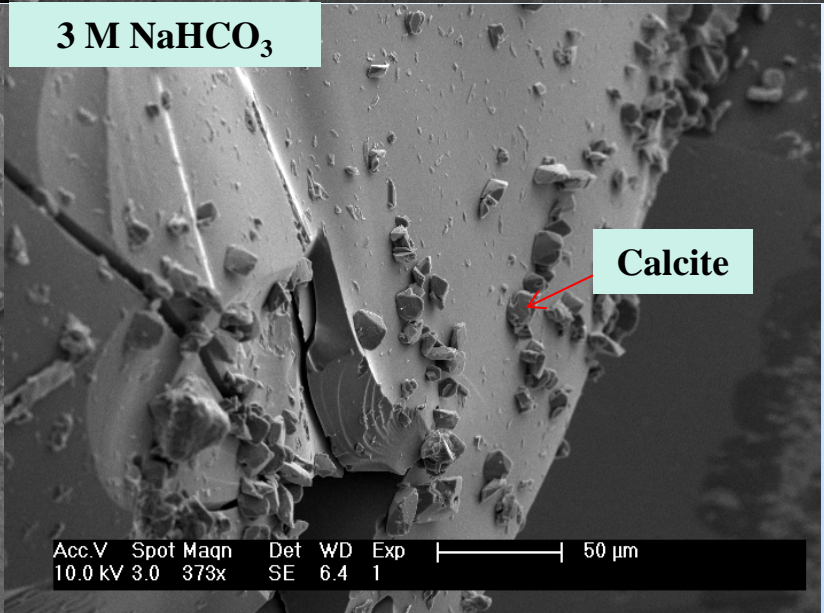
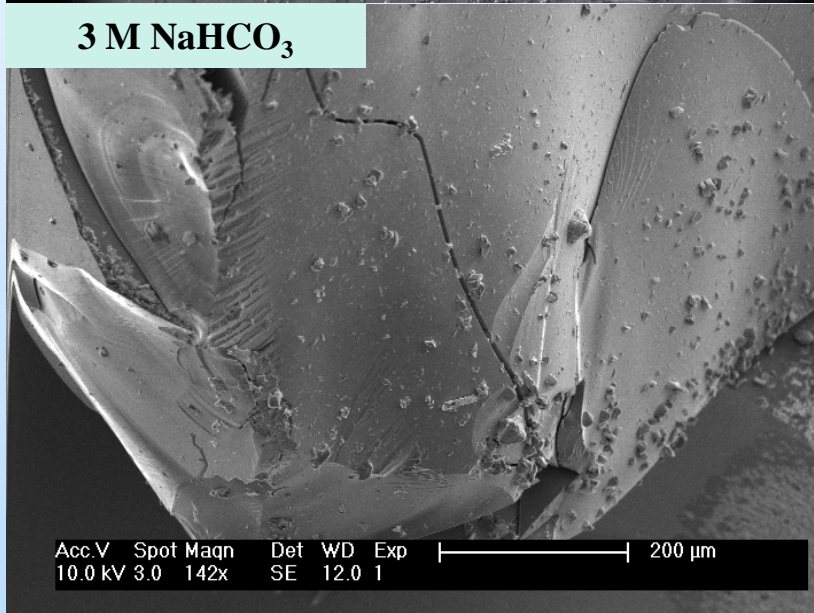
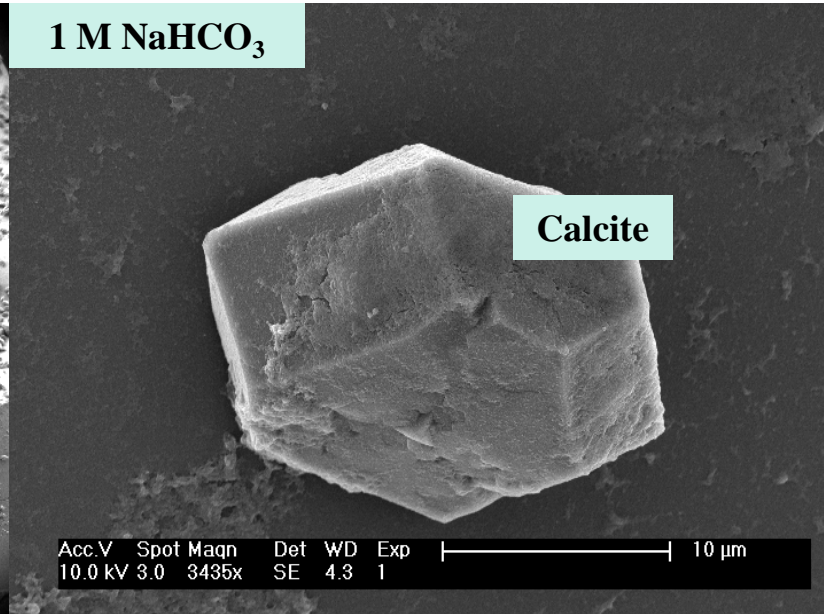
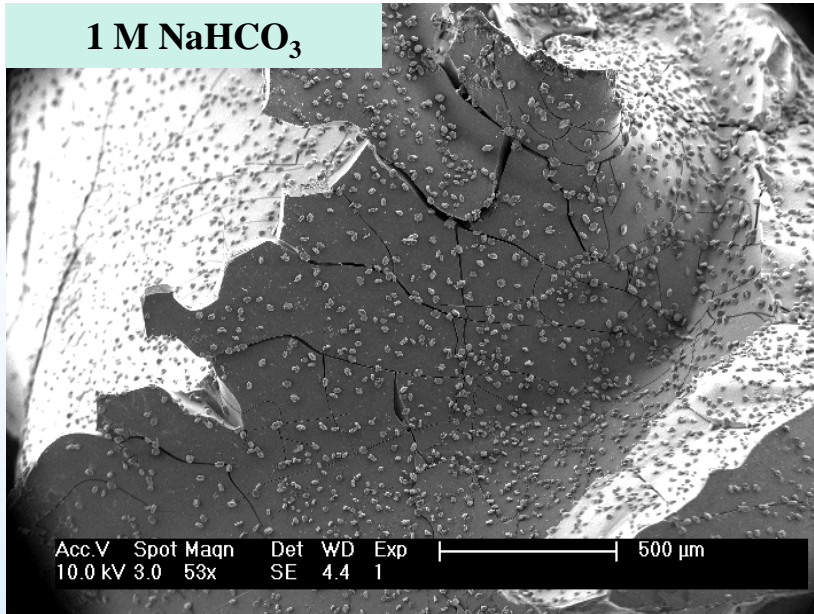
- Picture below: The surface of natural basalt chunk after the reaction.
Conditions: 200°C, 1650 psi (3 days),
244.120 mg grain + 0.45 ml 1N
NaHCO₃.



Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 2615x SE 8.5 1

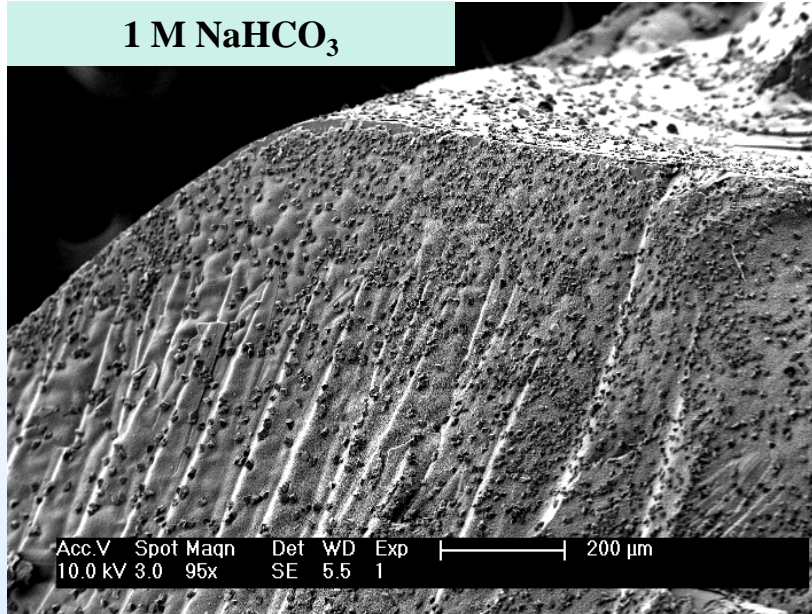
10 μm

Basaltic glass piece (made by melting Connecticut basalt)

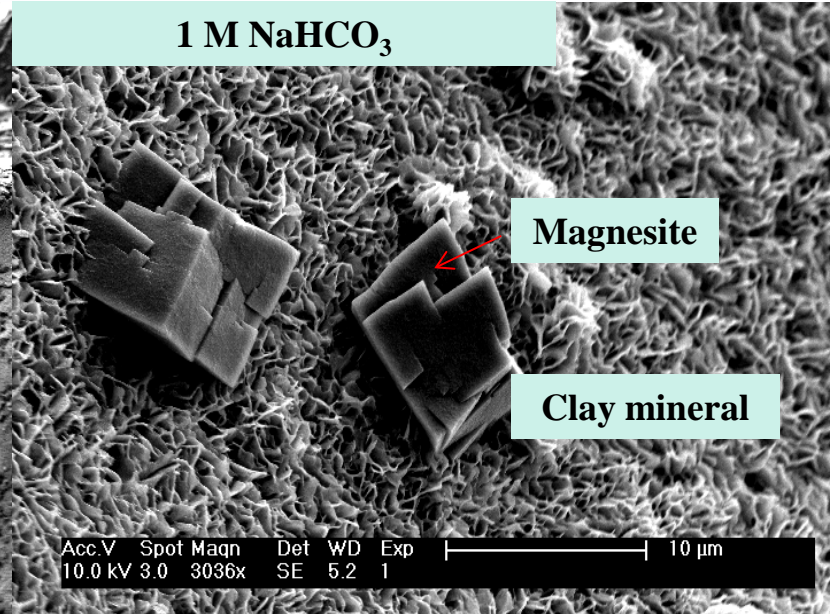


Basaltic glass (made by melting of Hawaiian picrite)

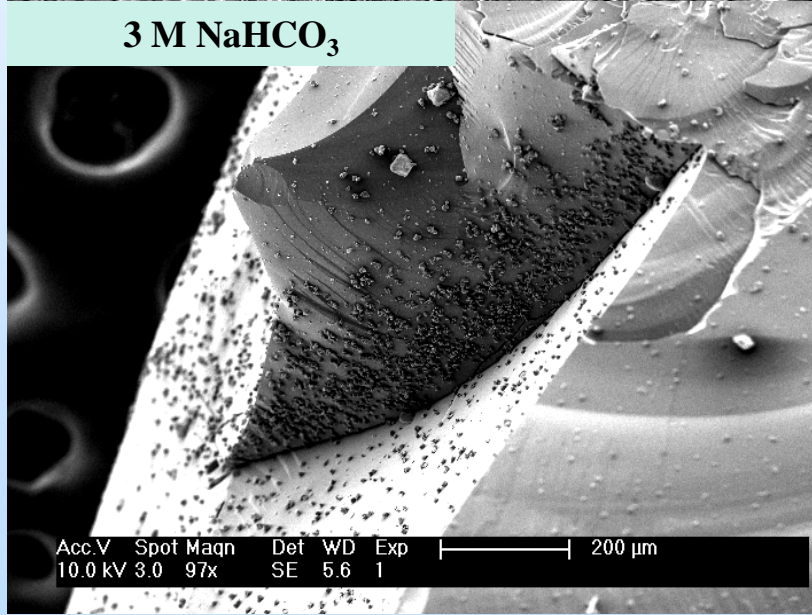
1 M NaHCO₃



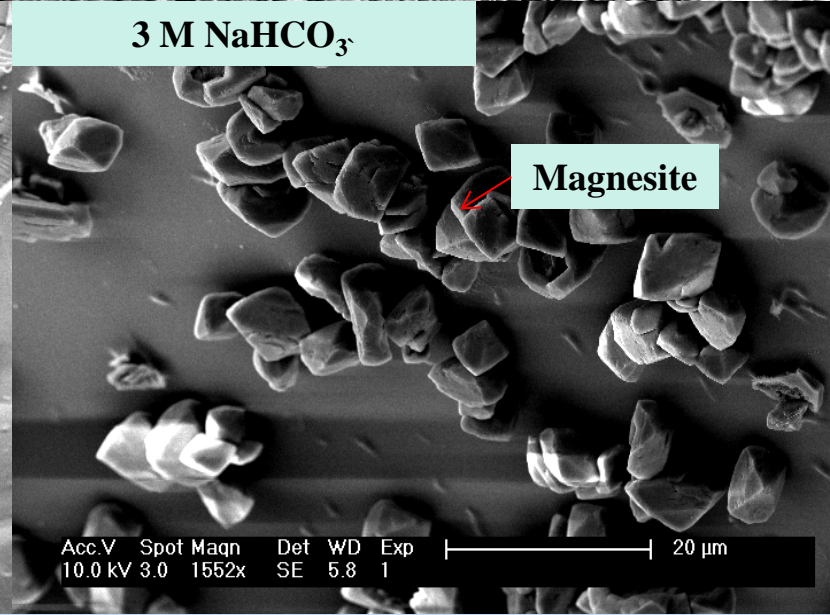
1 M NaHCO₃



3 M NaHCO₃



3 M NaHCO₃





Carbonation fraction (CF)

$$\text{Carbonation Fraction (CF)} = \frac{\Delta \text{DIC}}{M_{\text{olivine/basalt}}} \times 100$$

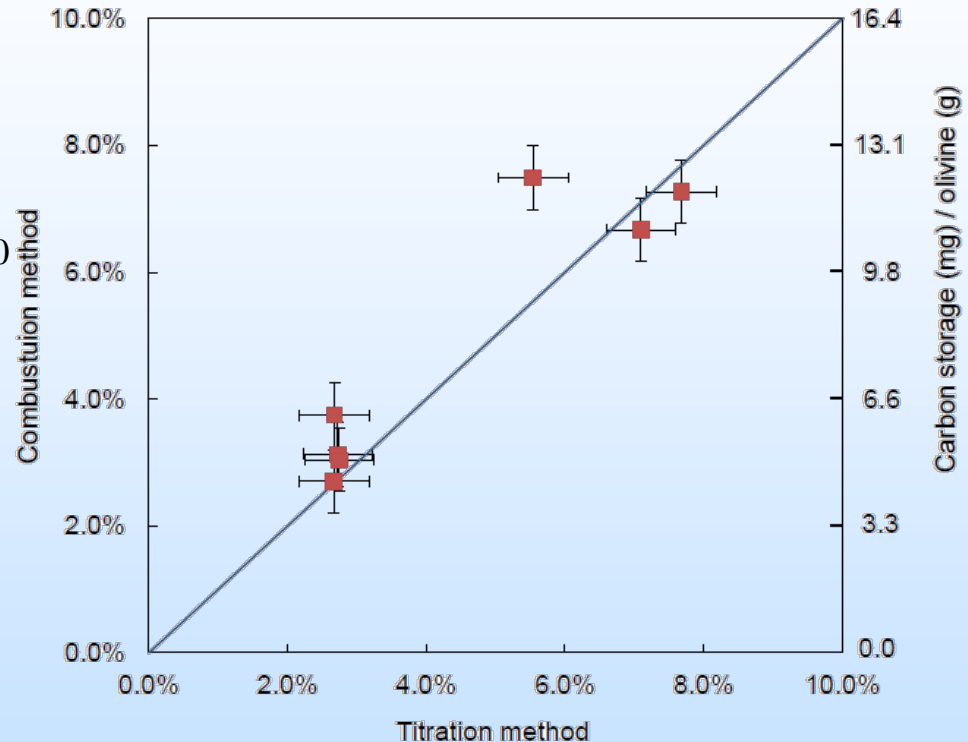
$$\text{Carbonation Fraction (CF)} = \frac{(M_{\text{Si}} \times 2 - M_{\text{Mg}^{2+}}) \times W_{\text{solution}}}{M_{\text{olivine/basalt}}} \times 100$$

ΔDIC represents the moles of DIC consumed in an experiment as formation of carbonates (i.e., MgCO_3 and FeCO_3).

$M_{\text{olivine/basalt}}$ are moles of divalent cations in the Olivine/basalt (including Fe^{2+} , Mg^{2+} , Ca^{2+}).

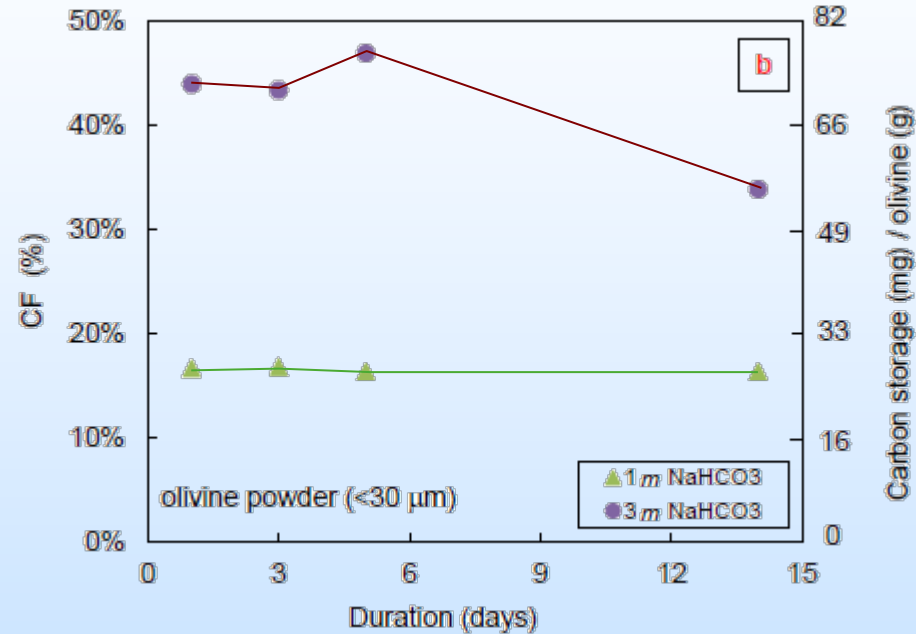
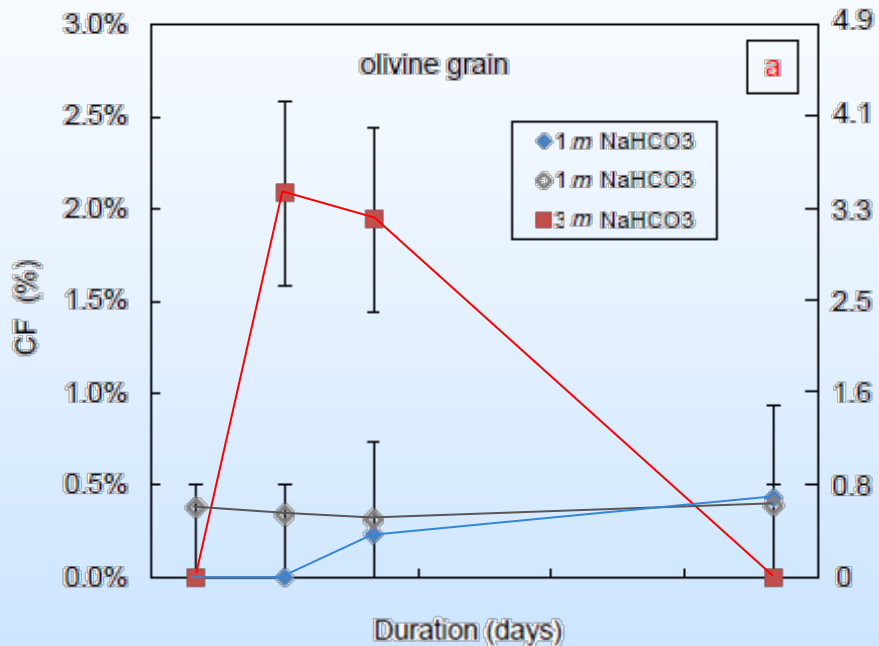
$$CS = CF \times \frac{12}{W_M} \times 2 \times 1000$$

W_M is the molecular weight of olivine, or average mass of the basalt that contains two moles of divalent cations





Carbonation fraction (CF)

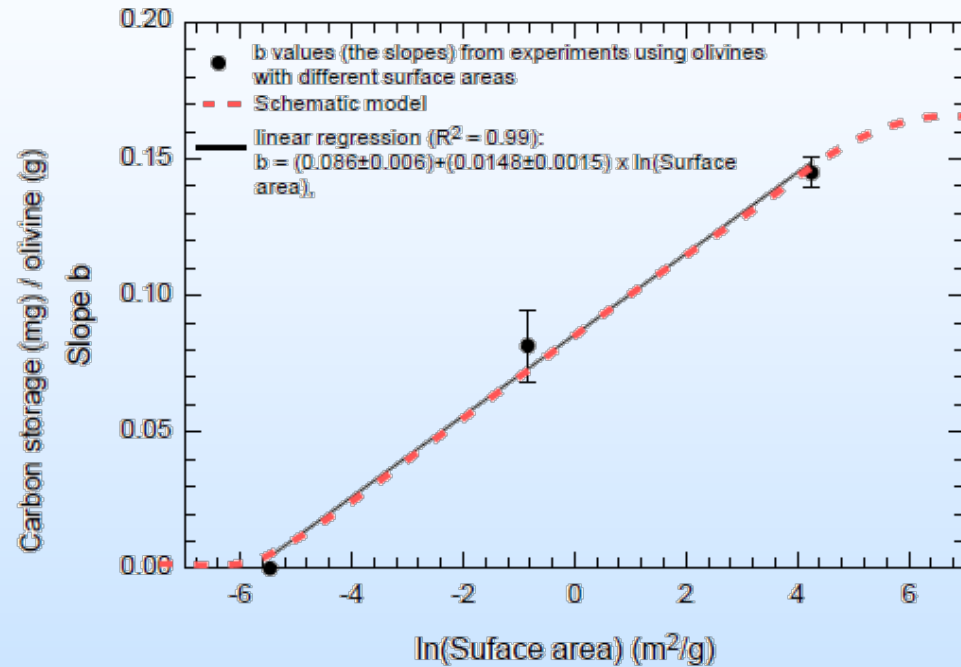
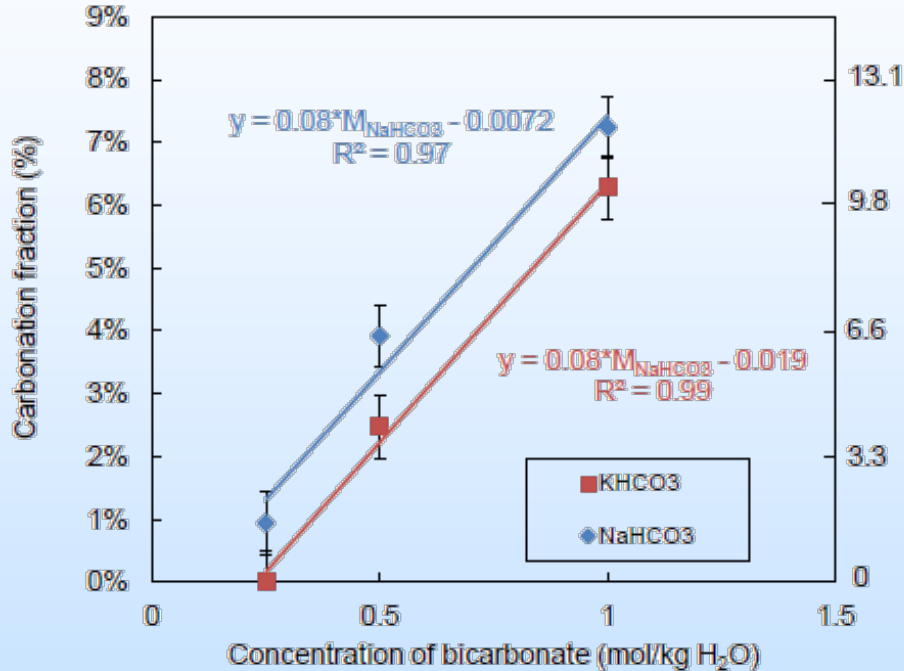


Questions:

1. Carbonation fraction increase with the concentration of NaHCO₃
2. Carbonation fraction rate is highest in the first couple of days, reach a plateau and then decrease with time
3. Carbonation fraction increase with decreasing grain size

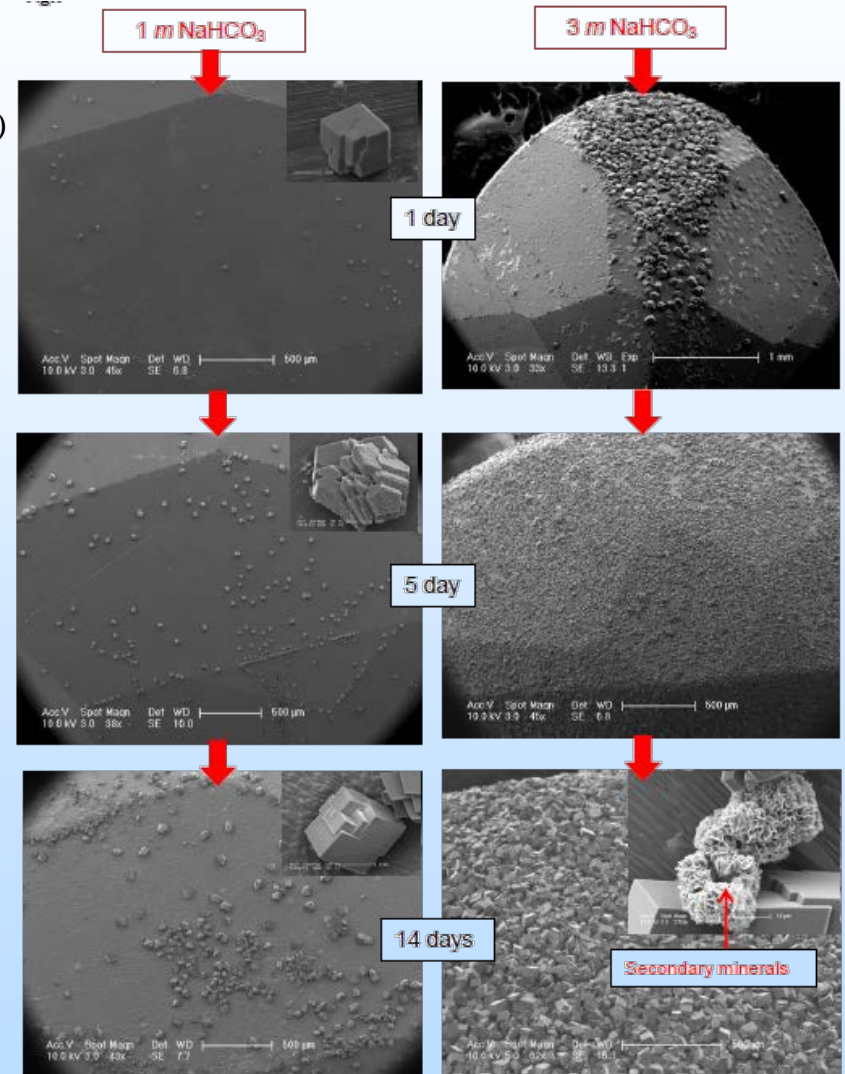
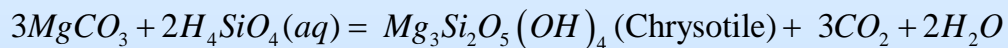
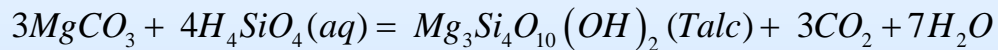
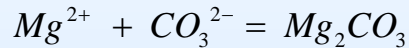
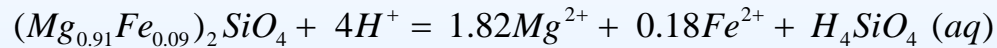
Effect of concentration of NaHCO_3 on Maximum carbonation fraction

olivine powder (~50 μm), 3days

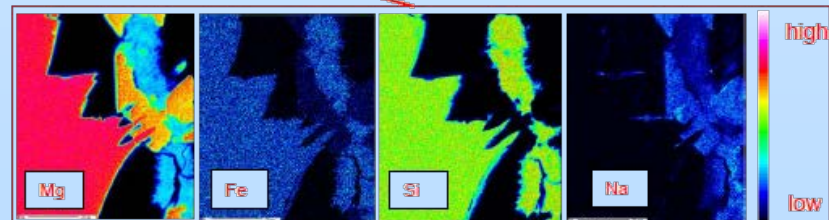
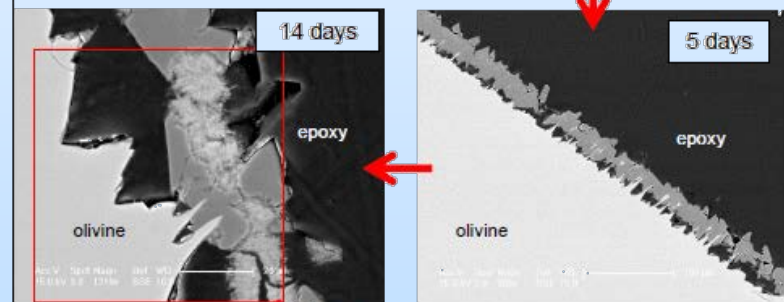
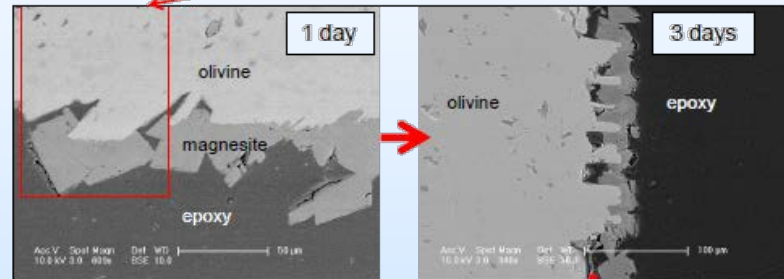
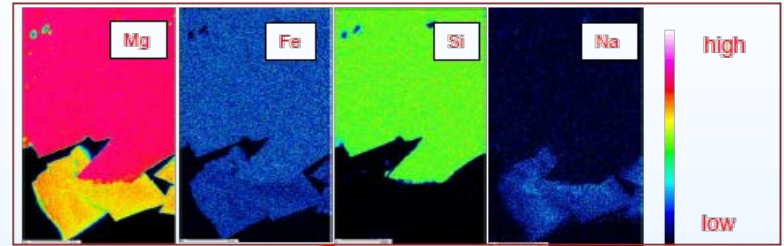
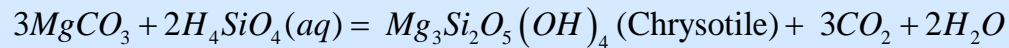
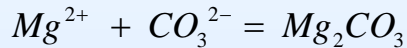
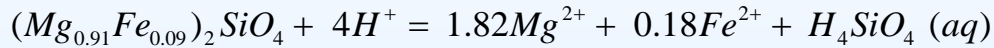


$$CF_{\max} = [(0.086 \pm 0.006) + (0.0148 \pm 0.0015) \times \ln(S)] \times m_{\text{DIC}} + a$$

Formation of secondary Mg-bearing silicate minerals

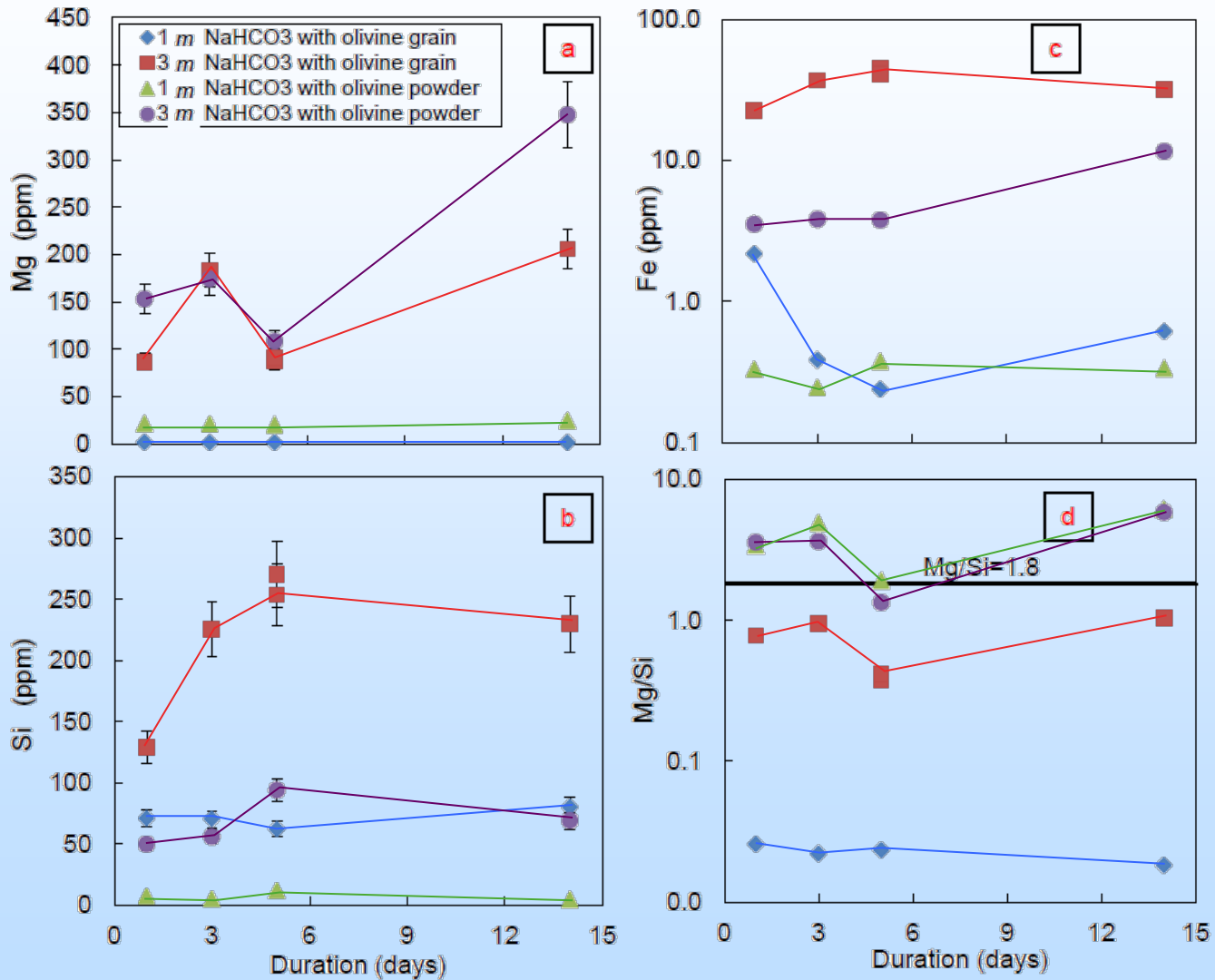


Formation of secondary Mg-bearing silicate minerals

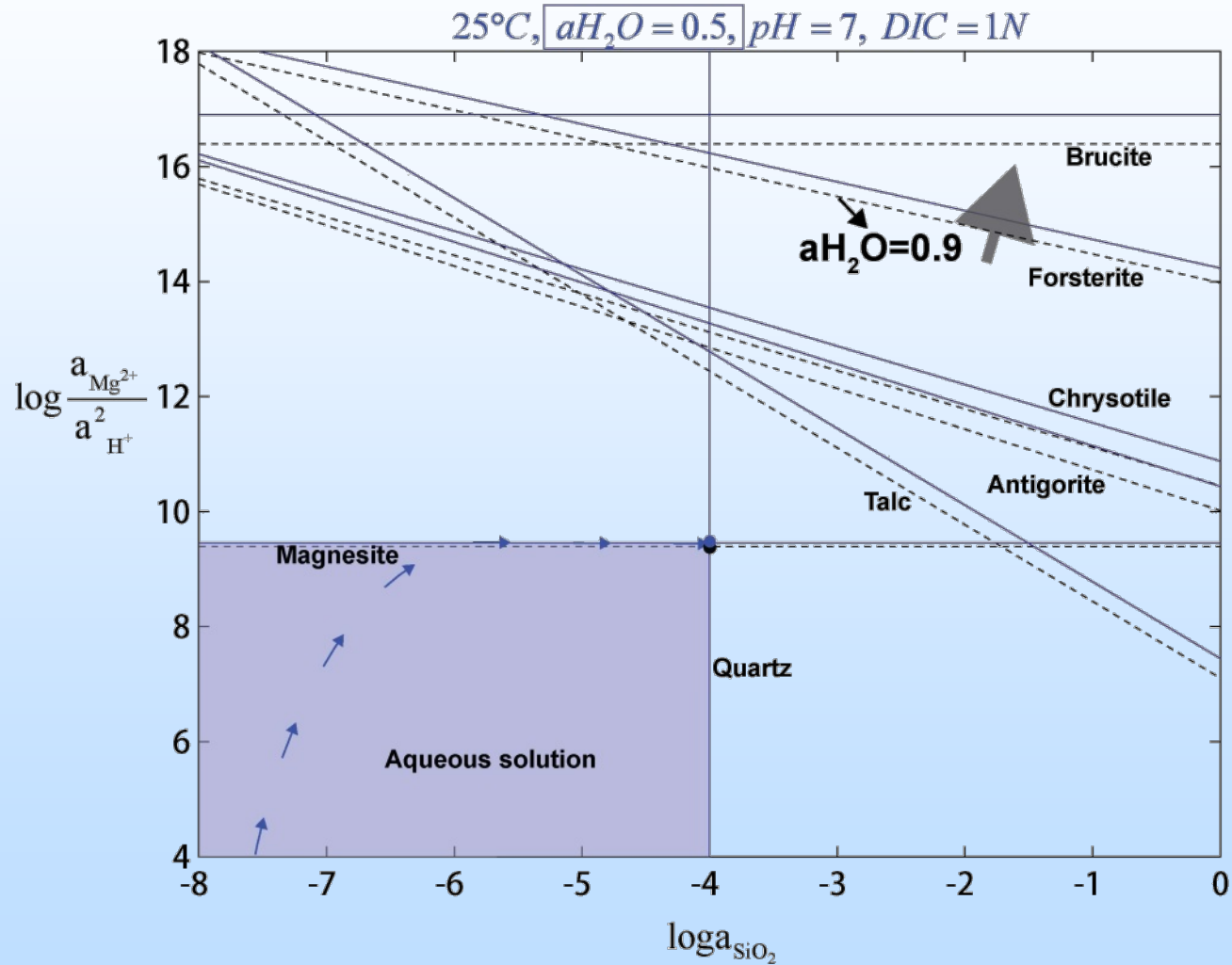




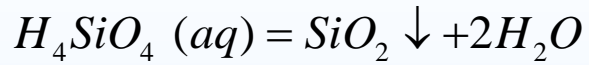
Formation of secondary Mg-bearing silicate minerals



Thermodynamic consideration

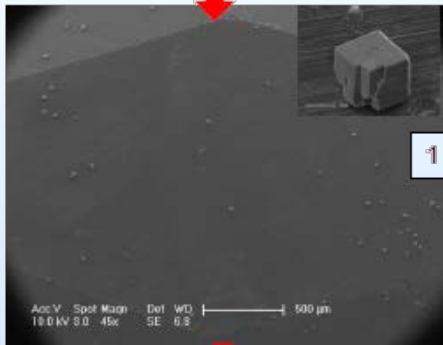


Experiments with different water/rock ratio



1 m NaHCO₃

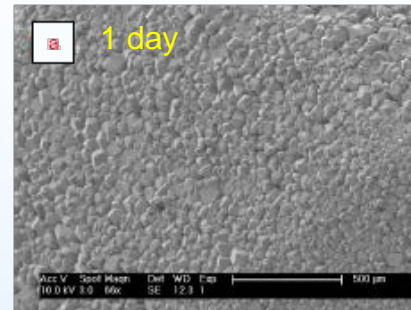
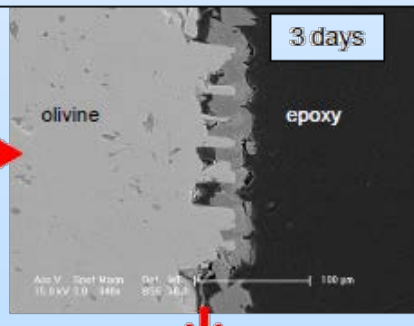
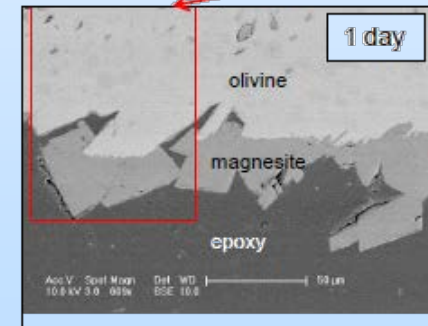
3 m NaHCO₃



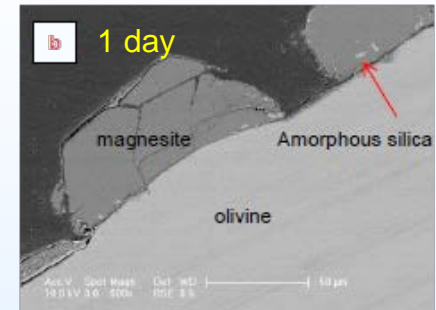
1 day

1 day

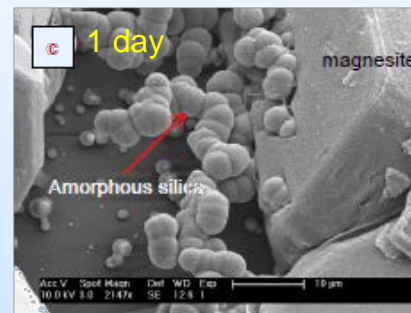
3 days



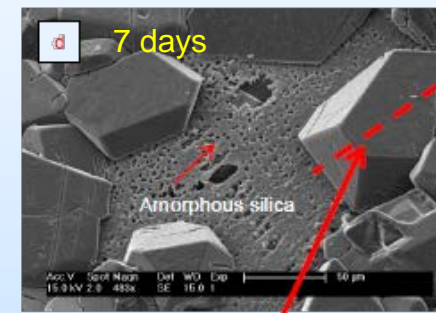
a 1 day



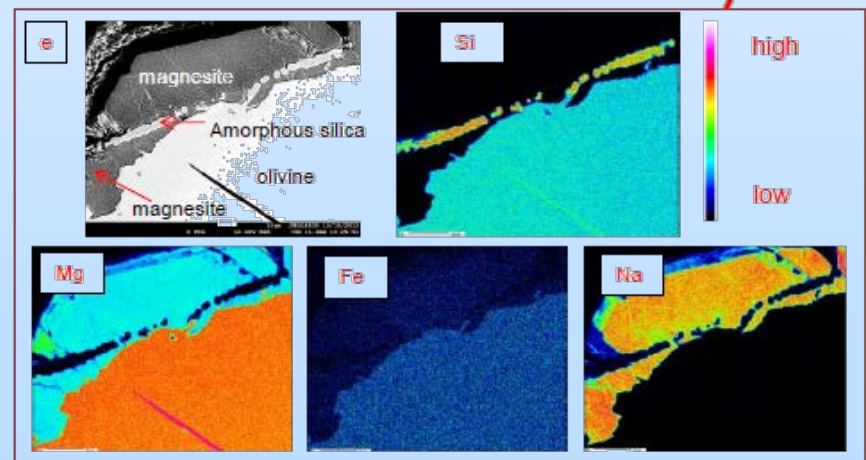
b 1 day



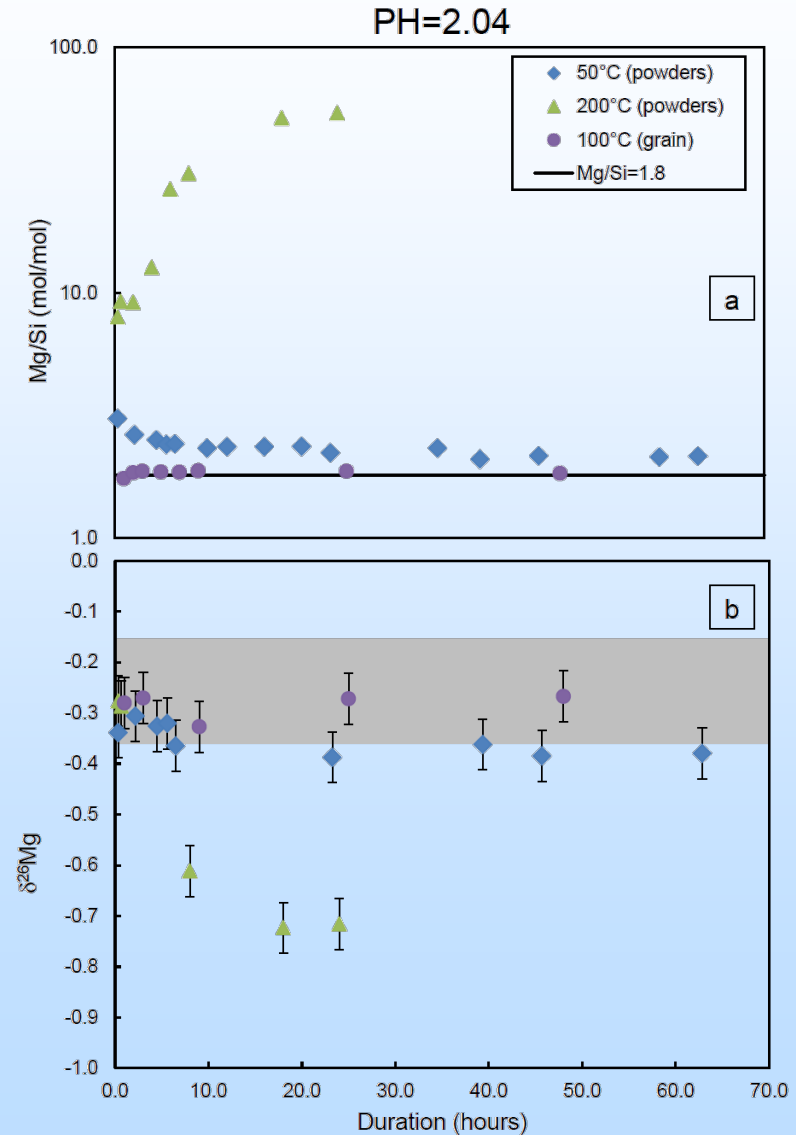
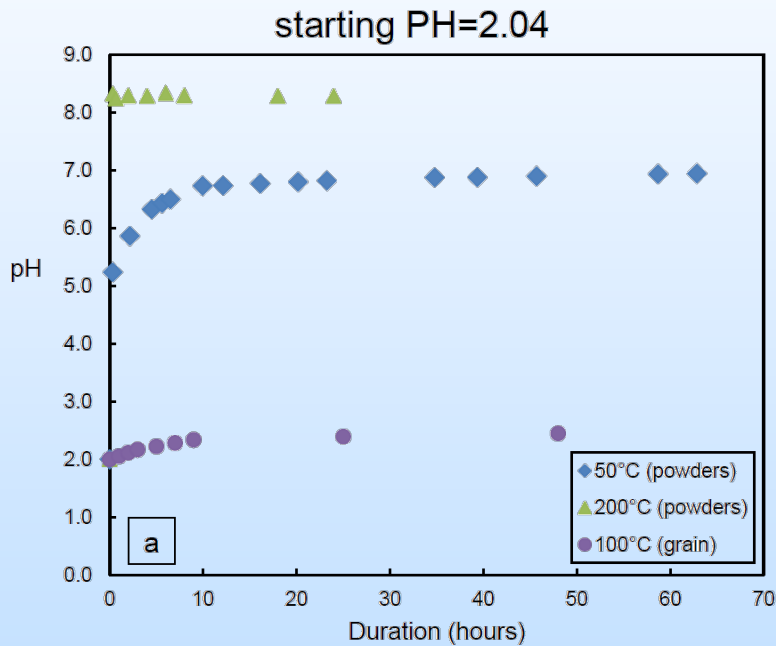
c 1 day



d 7 days

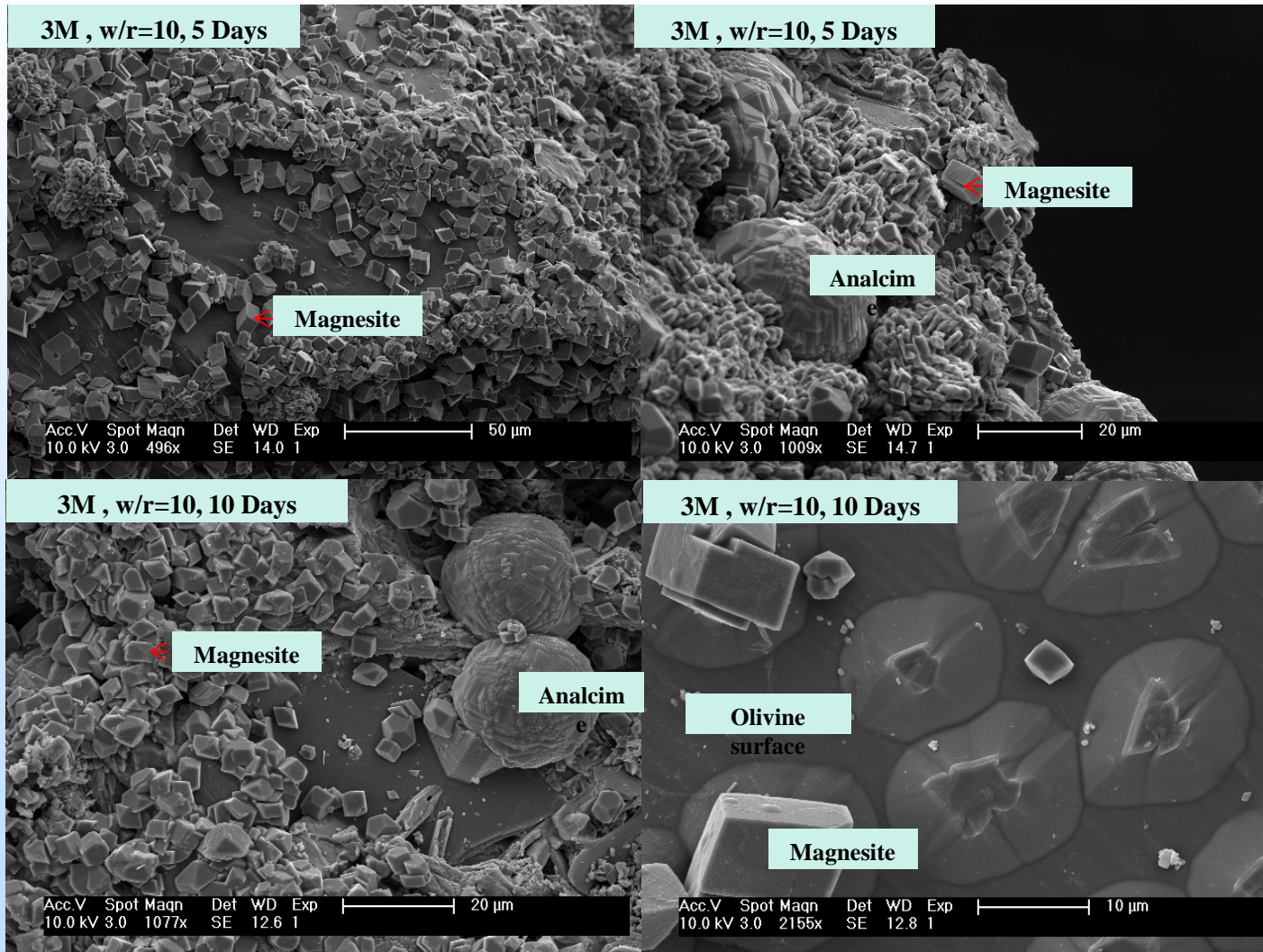


Mg isotope fractionation during dissolution



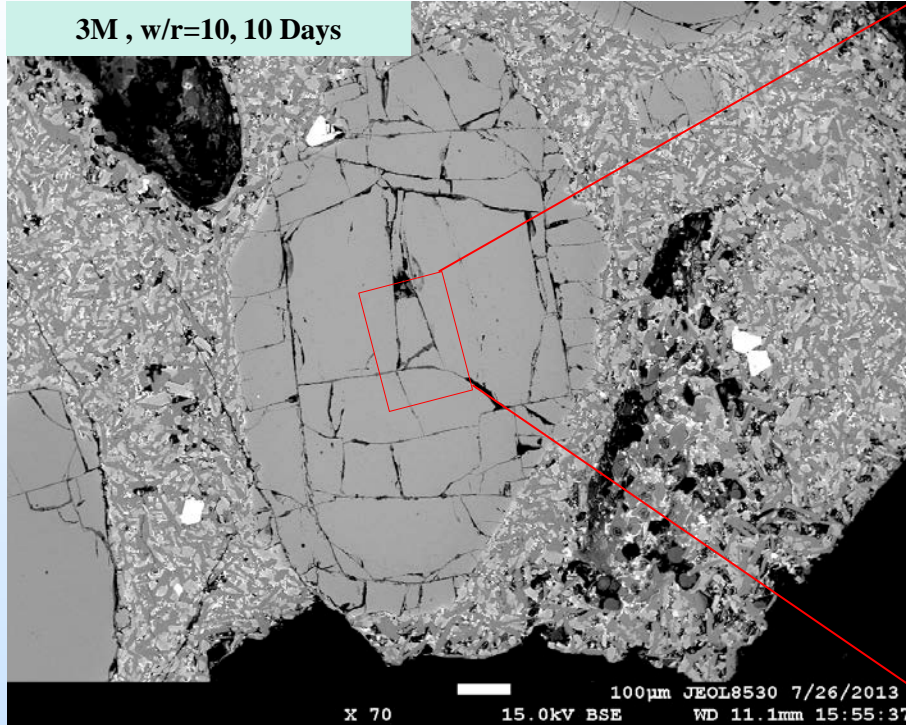


Scaling-up: reaction with picrite cube

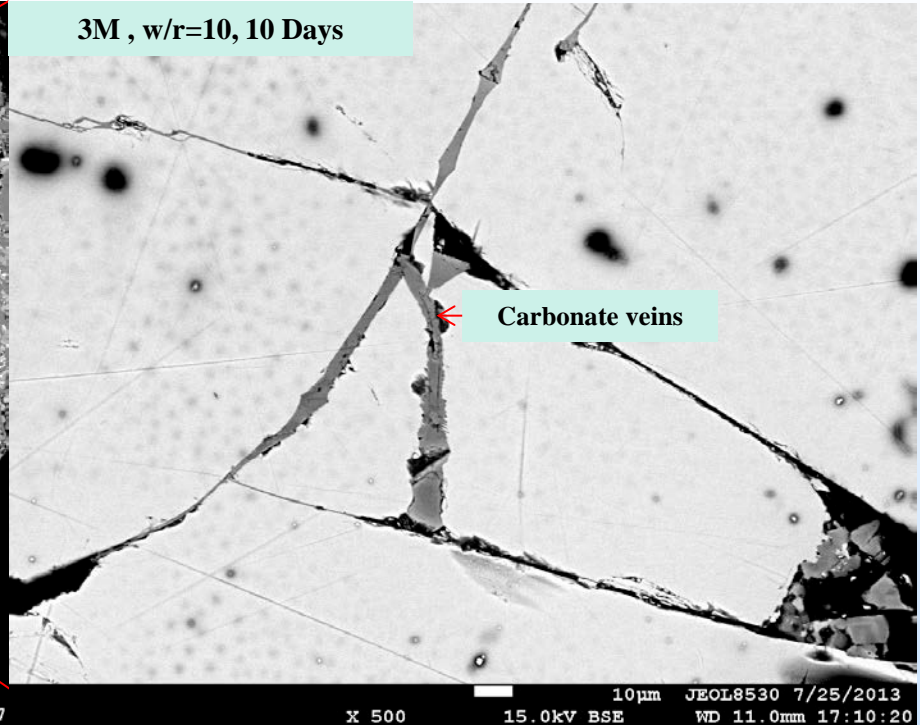


Scaling-up: reaction with picrite cube

3M , w/r=10, 10 Days



3M , w/r=10, 10 Days



The average composition of the carbonate veins:
Mg: 76.1%, Fe: 20.0%, Ca: 3.9% (magnesite)

Also, we see some zonation of the carbonate veins:
Darker core (more Mg) and brighter rim (more Fe)

Crack	Before reaction (μm)	After reaction filled with carbonates (μm)
Wide	3.33	8.75
Middle	1.35	5.03
Narrow	0.45	0.79

Carbonates formed in the olivine cracks could have widened the cracks.



Summary of geochemical result

- Olivine and basalts can form carbonates after reacting with CO₂-containing fluids in our experimental conditions, showing a big CCS potential.
- Reaction rates are faster at higher temperature, higher concentration of DIC in the fluid, and smaller grain-size of crystal.
- Reactions involving olivines are much faster than basalts.
- Carbonation rate after the-first-day reaction for both olivines and basalt determined in our studies is comparable to previous studies, but in our experiments the carbonation reaction for olivines proceeds slowly after the first day.
- The limitation of the carbonation reaction is the production of secondary Mg-bearing silicate minerals, effective removal of SiO₂ from the solution is essential to the carbonation efficiency.
- Basaltic glasses also exhibit fast reaction rate.
- The cracks in olivine grains of picrite chips have been observed to open up after reaction and filled with magnesites.

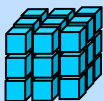


Geochemical modeling

KINFLOW: Aqueous phase reactive transport model in porous media with **kinetic** control of mineral reactions

MAIN FEATURES:

- **Aqueous and vapor phase non-isothermal flow and transport**
- **Mineral** dissolutions and precipitation via experimental **kinetics**
- **48 Minerals** covering major rock types and secondary minerals
- **30 Speciation** reactions in solution in **equilibrium** via EQ3/6, from 0-300°C
- **70 Aqueous Species**
- **Fe³⁺/Fe²⁺ Redox** reactions
- **Partitioning** between vapor and aqueous phases (O₂, CO₂, H₂O, ...)
- **Injection of fluids**
- **Dynamic porosity evolution. compaction**
- **0D, 1D, 2D**
- Sub-grid-scale **grain models** for mineral surface areas, volumes, porosity

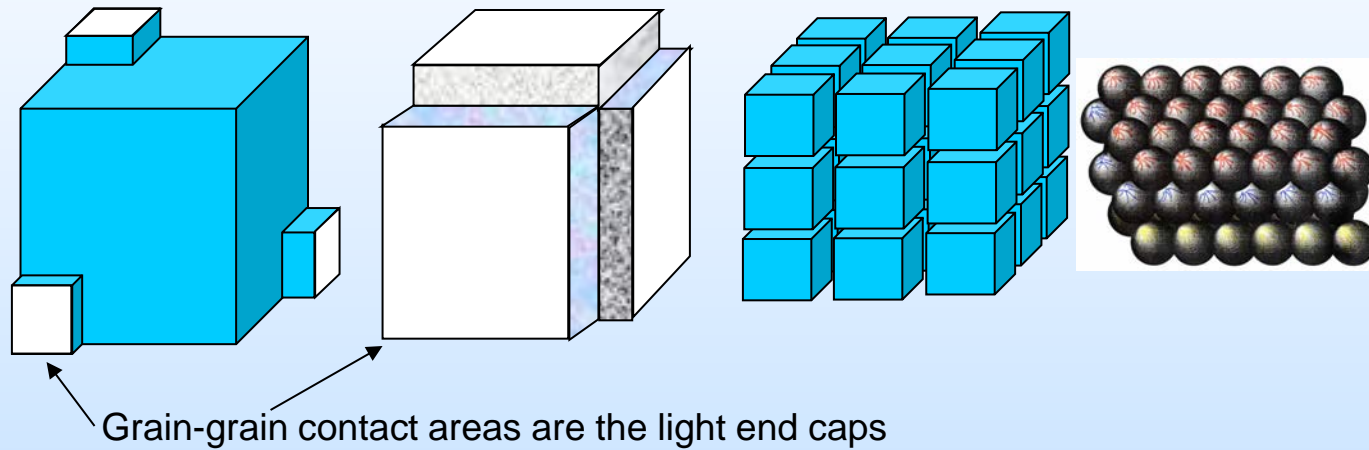


Any rectangular solid prism



Geochemical modeling

Grain models



Grain model parameters for fluid flow and mineral reaction kinetics: Grain volumes, spacing, porosity, surface areas, fluid gap spacing, and the permeability.

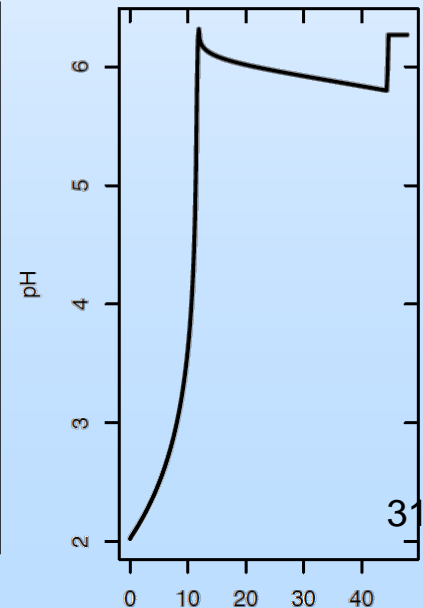
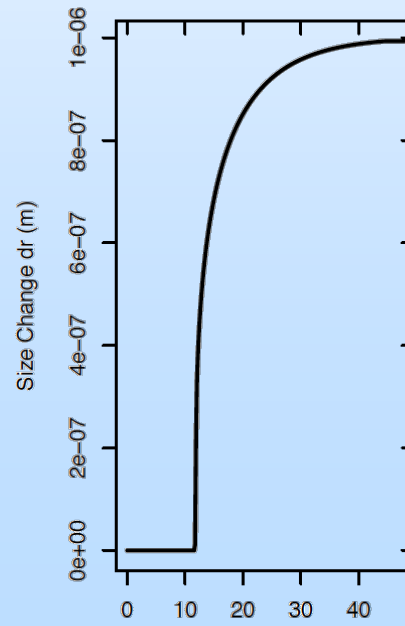
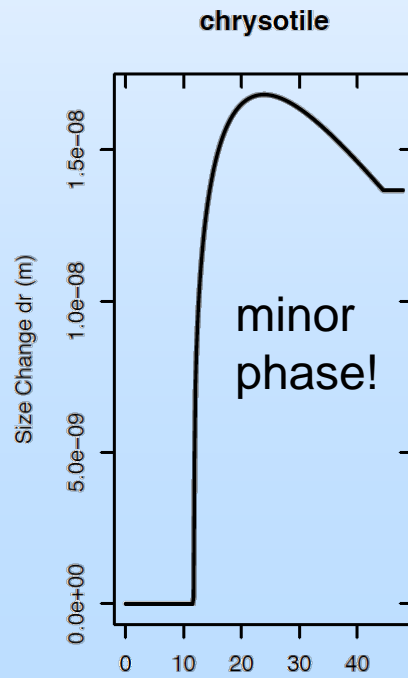
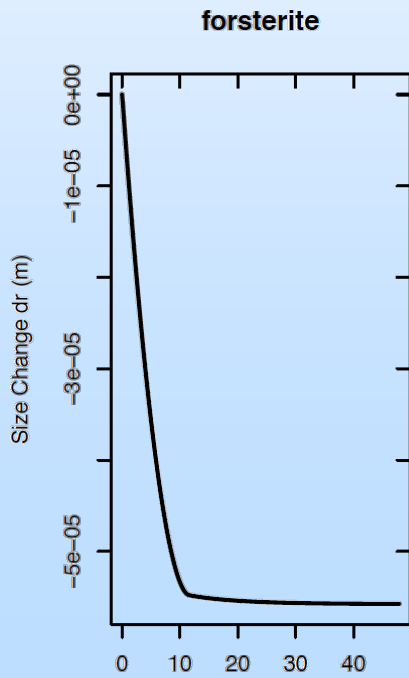
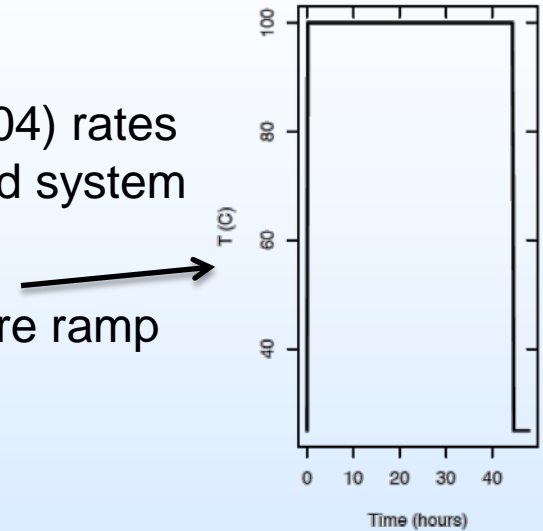


Geochemical modeling

Example for dissolution reaction

- Full model (KINFLOW) with Palandri and Kharaka (2004) rates
- Forsterite single crystal dissolution at 100°C in a closed system

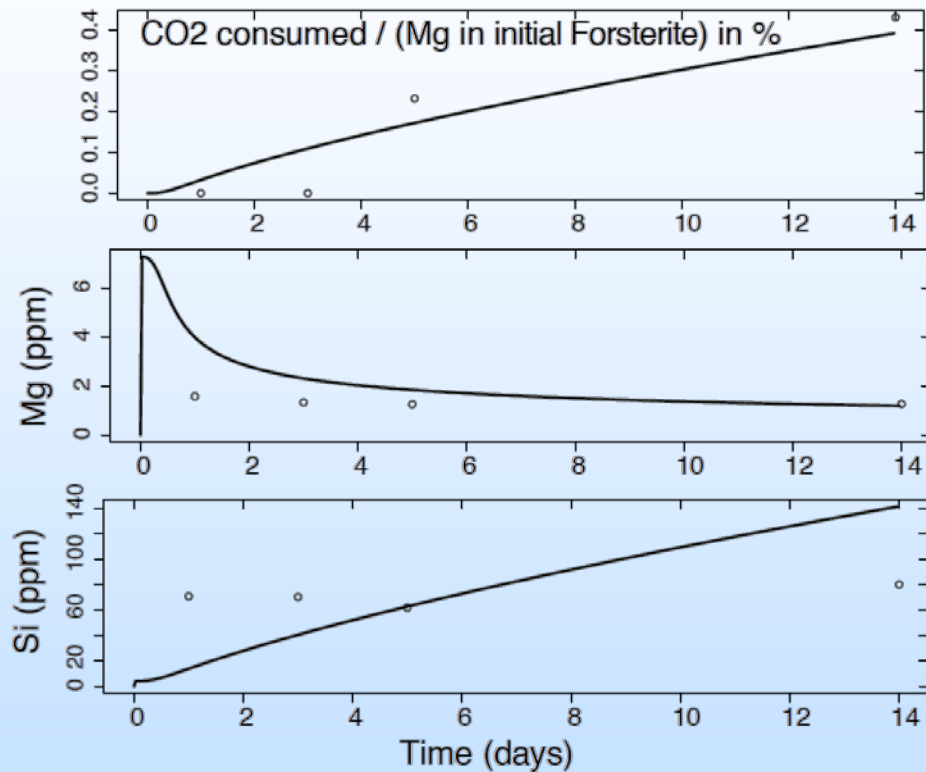
Temperature ramp





Geochemical modeling

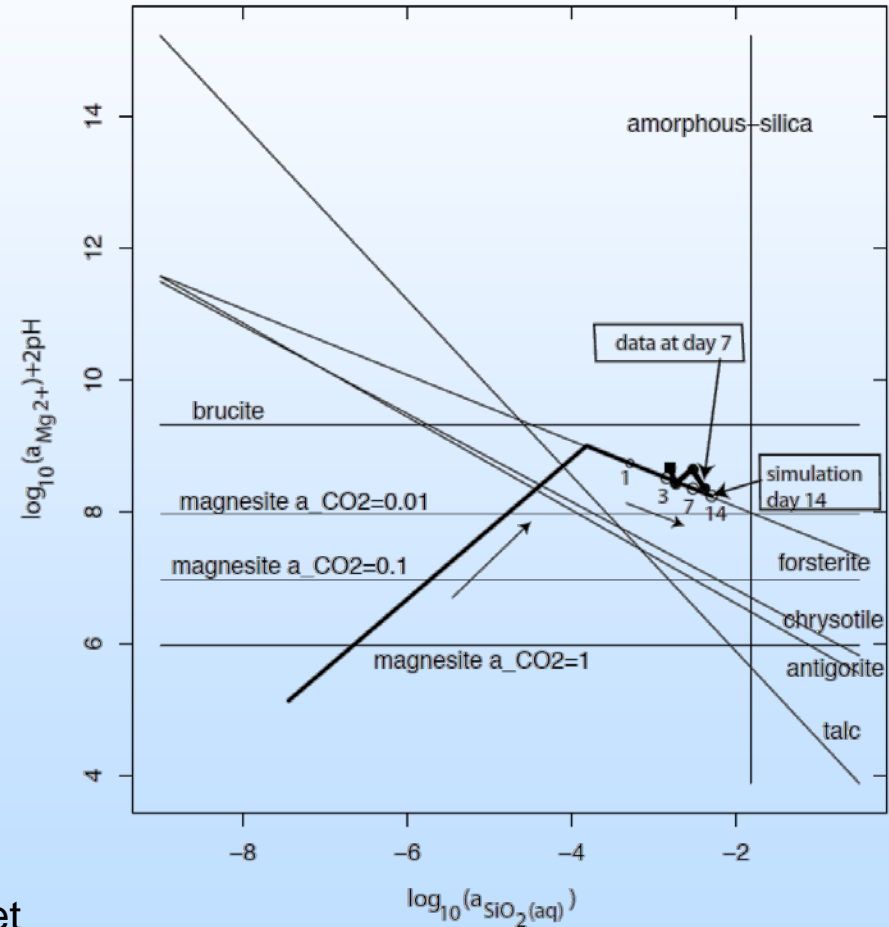
Model vs. Experimental Data



Olivine grain, 1 M NaHCO₃, 200 °C and 150 bar

Using magnesite precipitation kinetics from Saldi et al., (2010, 2012)

mineral equilibria at T=200 C, p=150 bars
simulation curve in bold



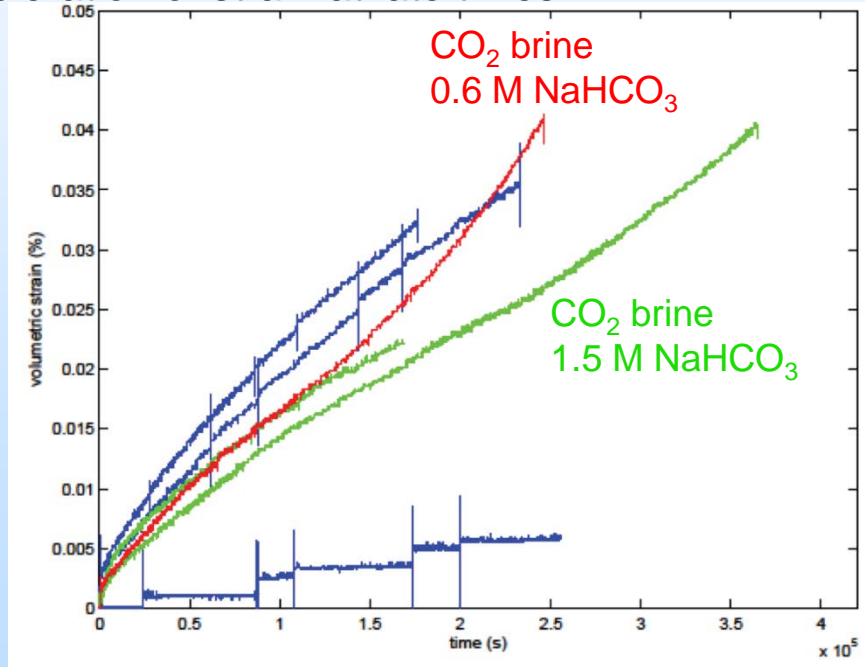


Geo-mechanical experiment and modeling



Reactive Flow Combined with Deformation

Dunite (olivine) samples saturated with different pore fluids are subjected to hydrostatic compaction (5 MPa, 150°C), followed by longitudinal deformation at constant strain rate. Samples reacted with CO₂ brine show an acceleration of strain at late times.



Volumetric strain curve fit with a hybrid creep model with 2 time scales (Main, 2000)

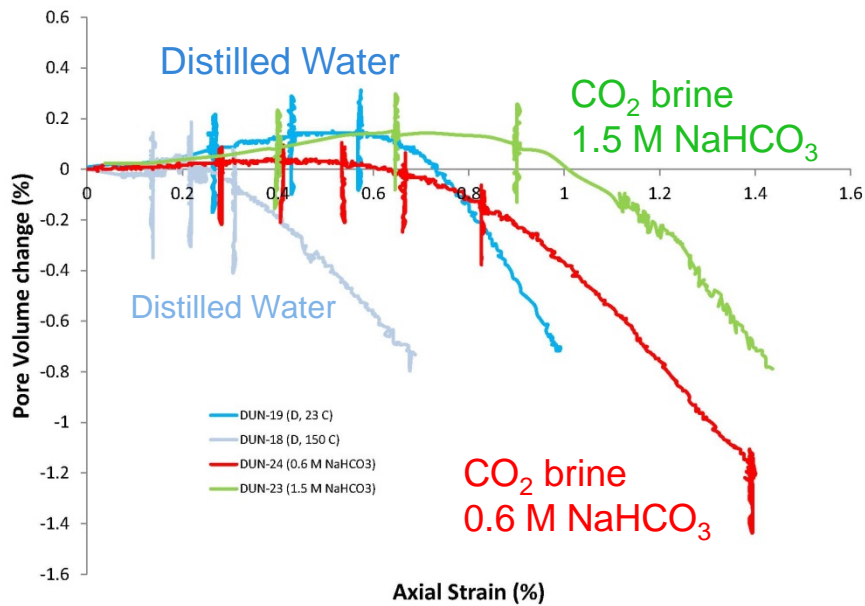


Geo-mechanical experiment and modeling

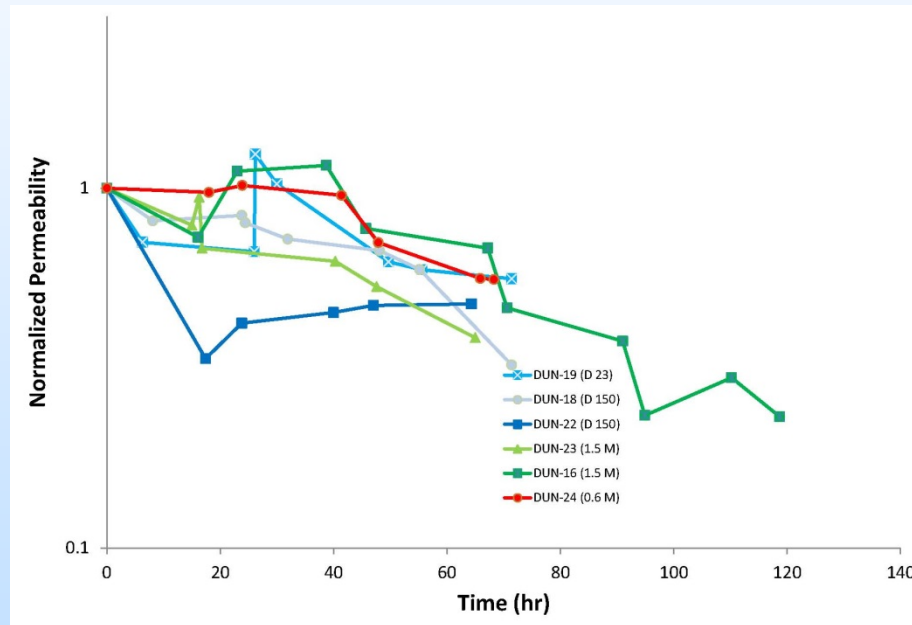
Reactive Flow Combined with Deformation

Dunite (olivine) samples saturated with different pore fluids are subjected to hydrostatic compaction (5 MPa, 150°C), followed by longitudinal deformation at constant strain rate.

Samples reacted with CO₂ brine accommodate more shortening before dilation and failure.



Pore volume change versus time for hydrostatic creep tests

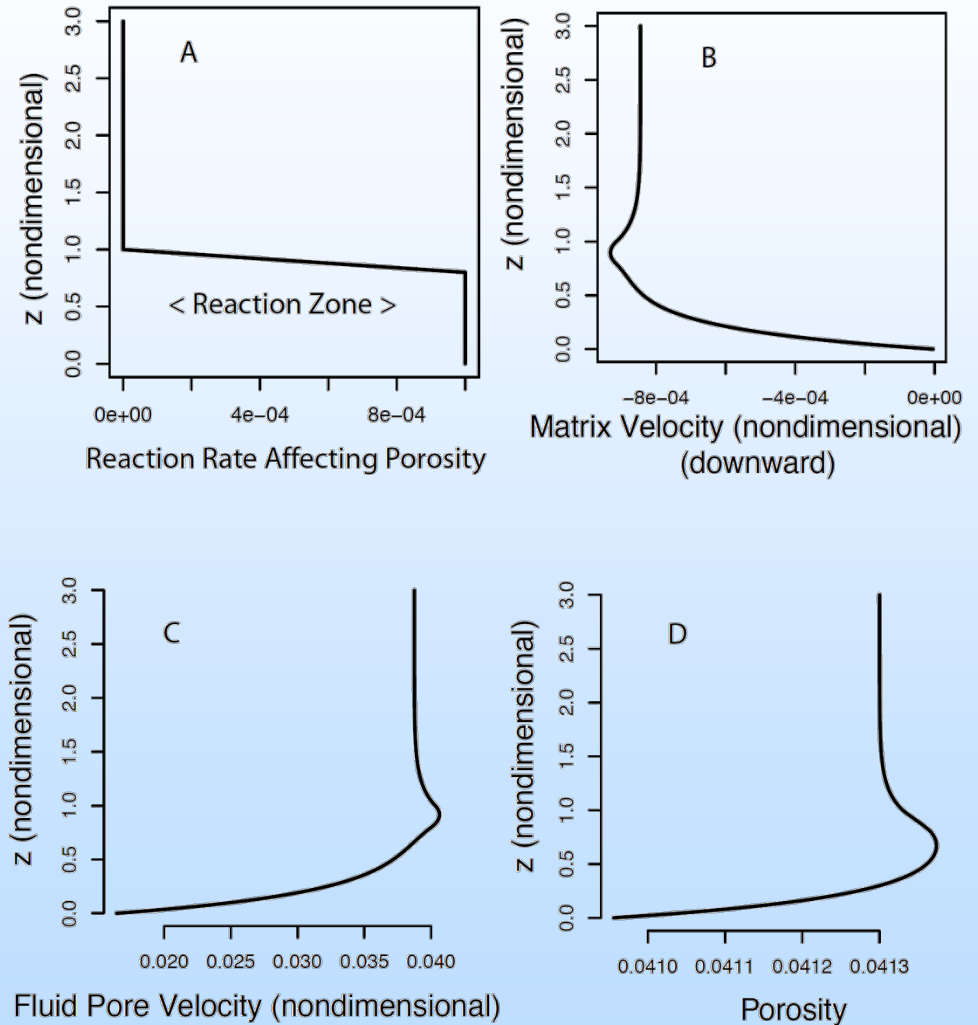


Permeability versus time for strain for hydrostatic creep tests (starting permeability = 1)



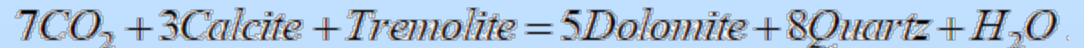
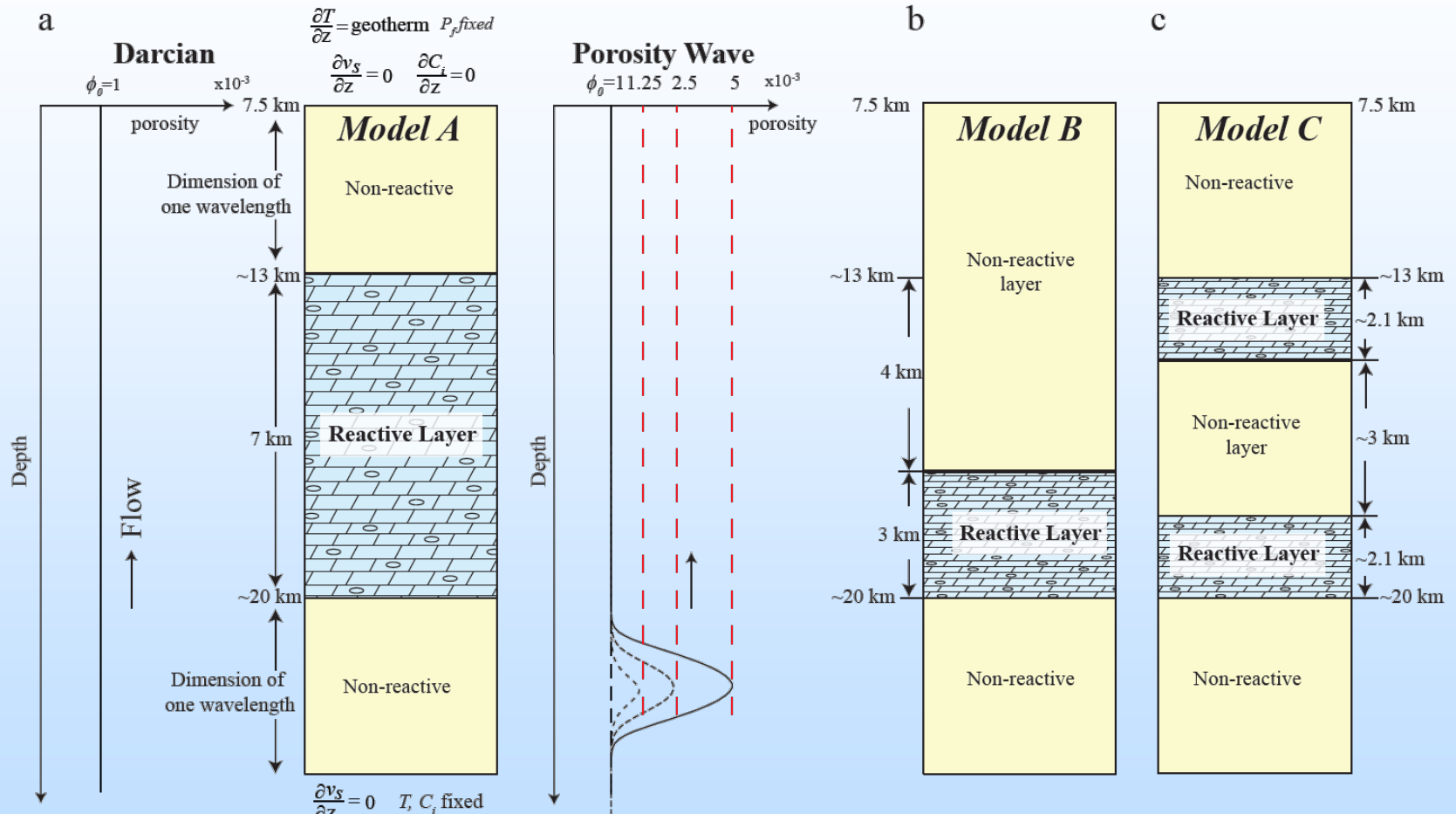
Geomechanical modeling: compaction

One-dimensional formulation for compaction of the solid phase with reactions between the solid and liquid phases



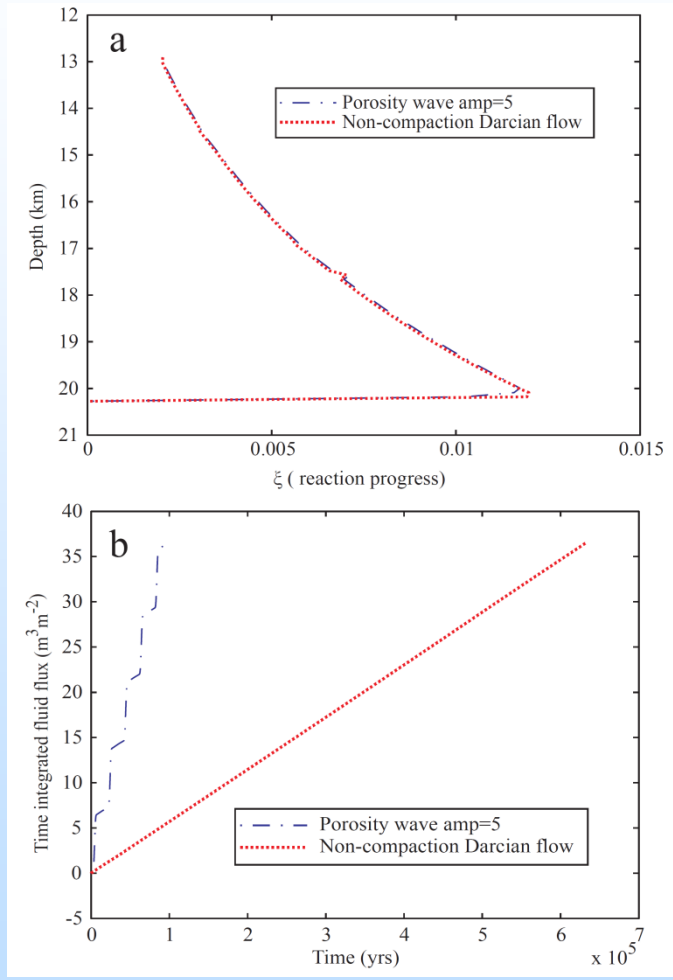
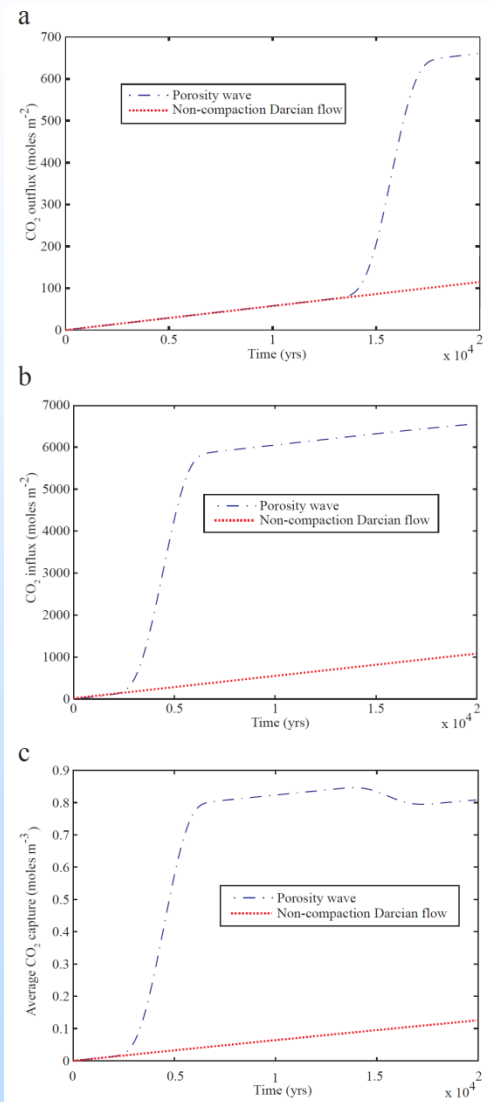
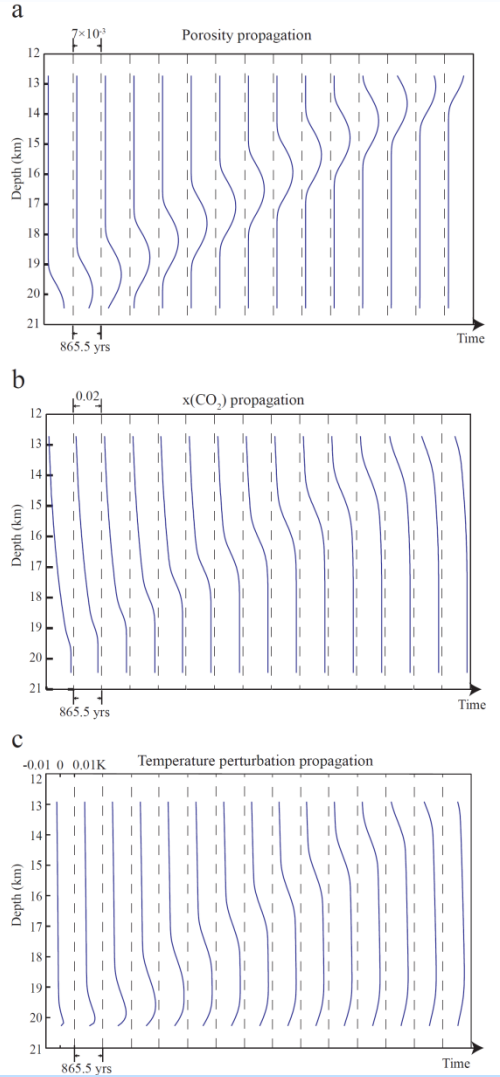


Geomechanical modeling: porosity wave





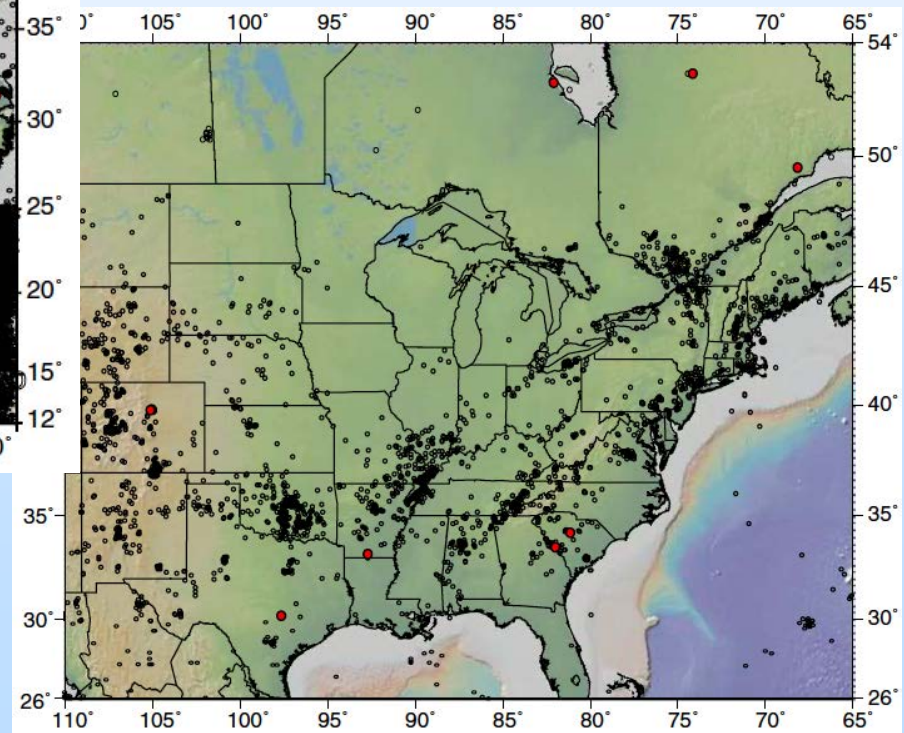
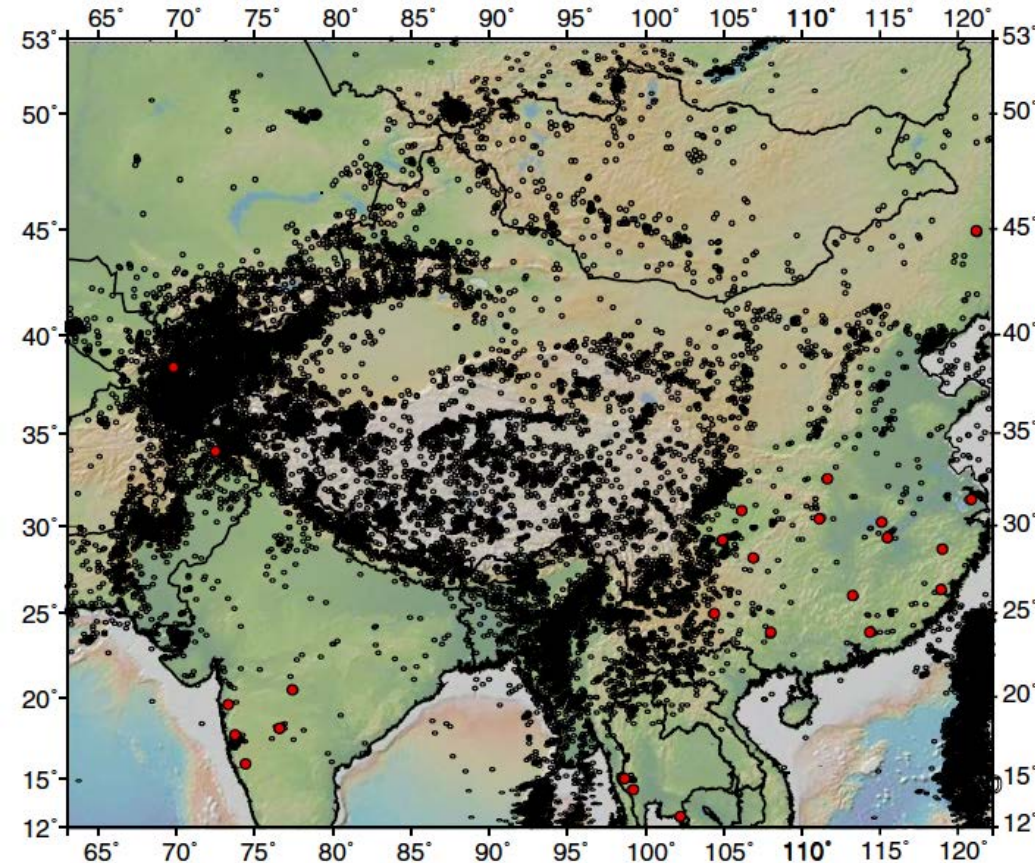
Geomechanical modeling: porosity wave





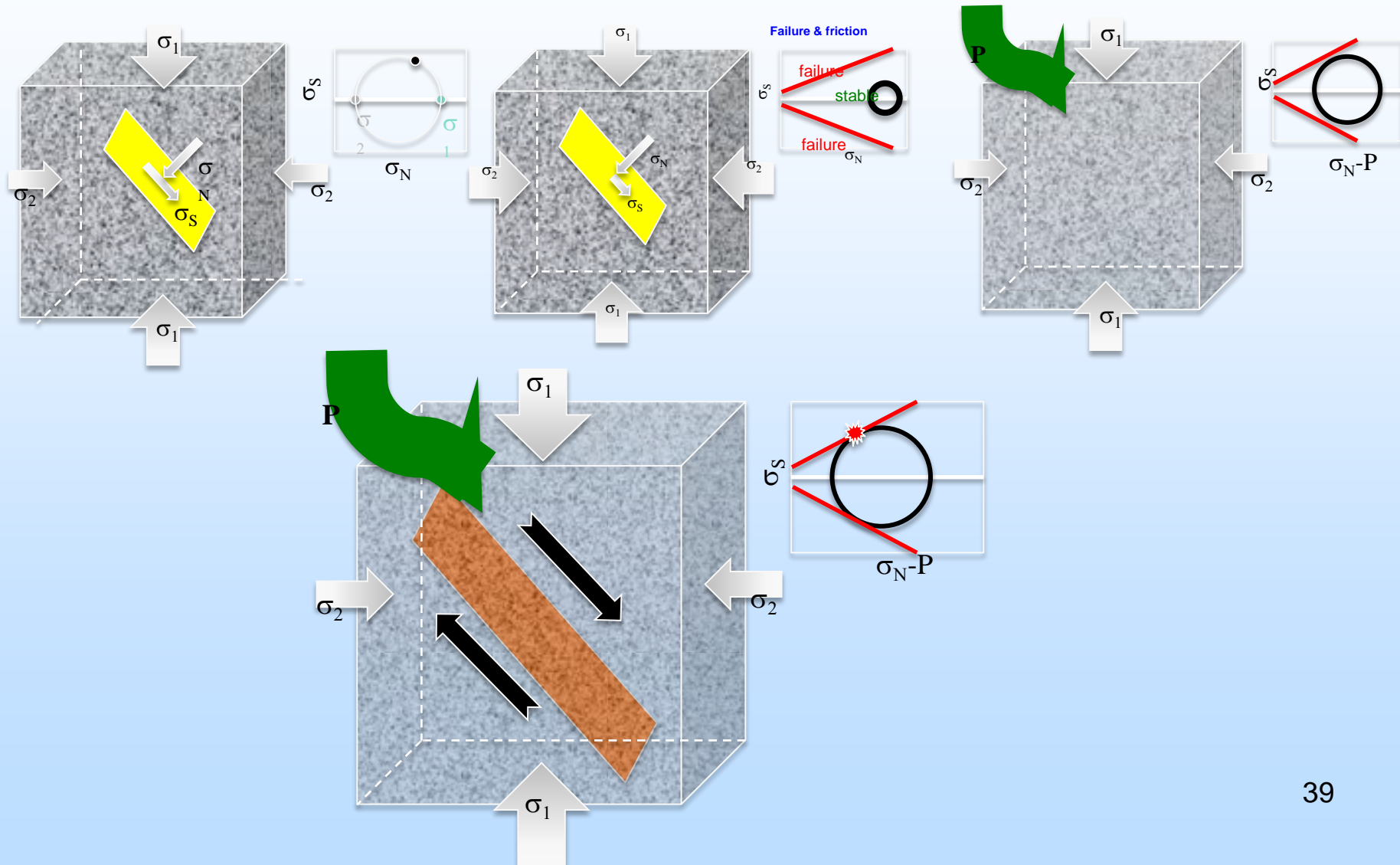
Mineral carbon sequestration and induced seismicity

Instrumentally recorded seismicity of south and east Asia, central and eastern United States and southeastern Canada. Red dots indicate sites of reservoir-induced seismicity.



CCS fluid injection needed to offset CO₂ emissions would trigger at least low level of seismicity and compromise cap rock -
Zoback & Gorelick, PNAS, 2012

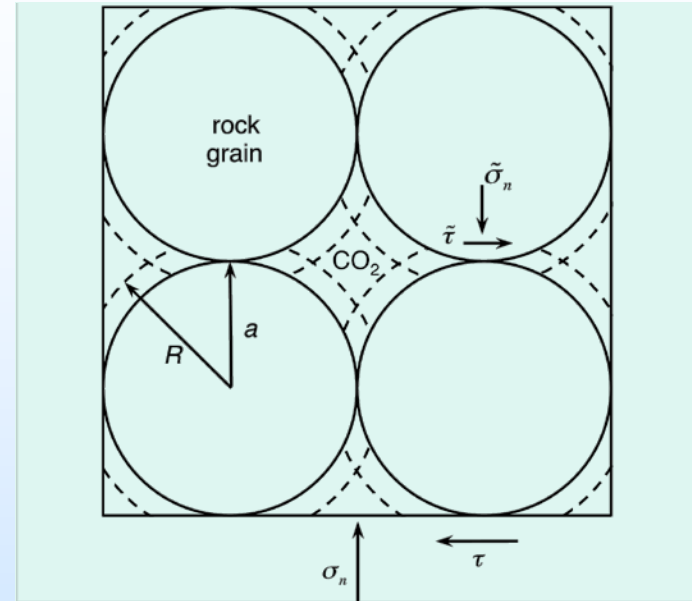
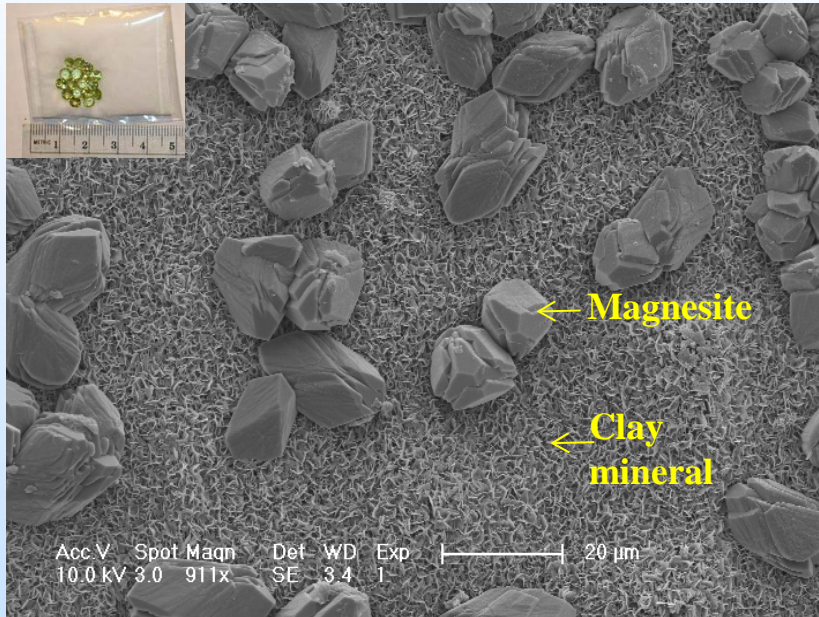
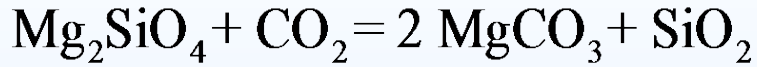
Mineral carbon sequestration and induced seismicity





Mineral carbonation in mafic rocks

Carbonation of olivine:

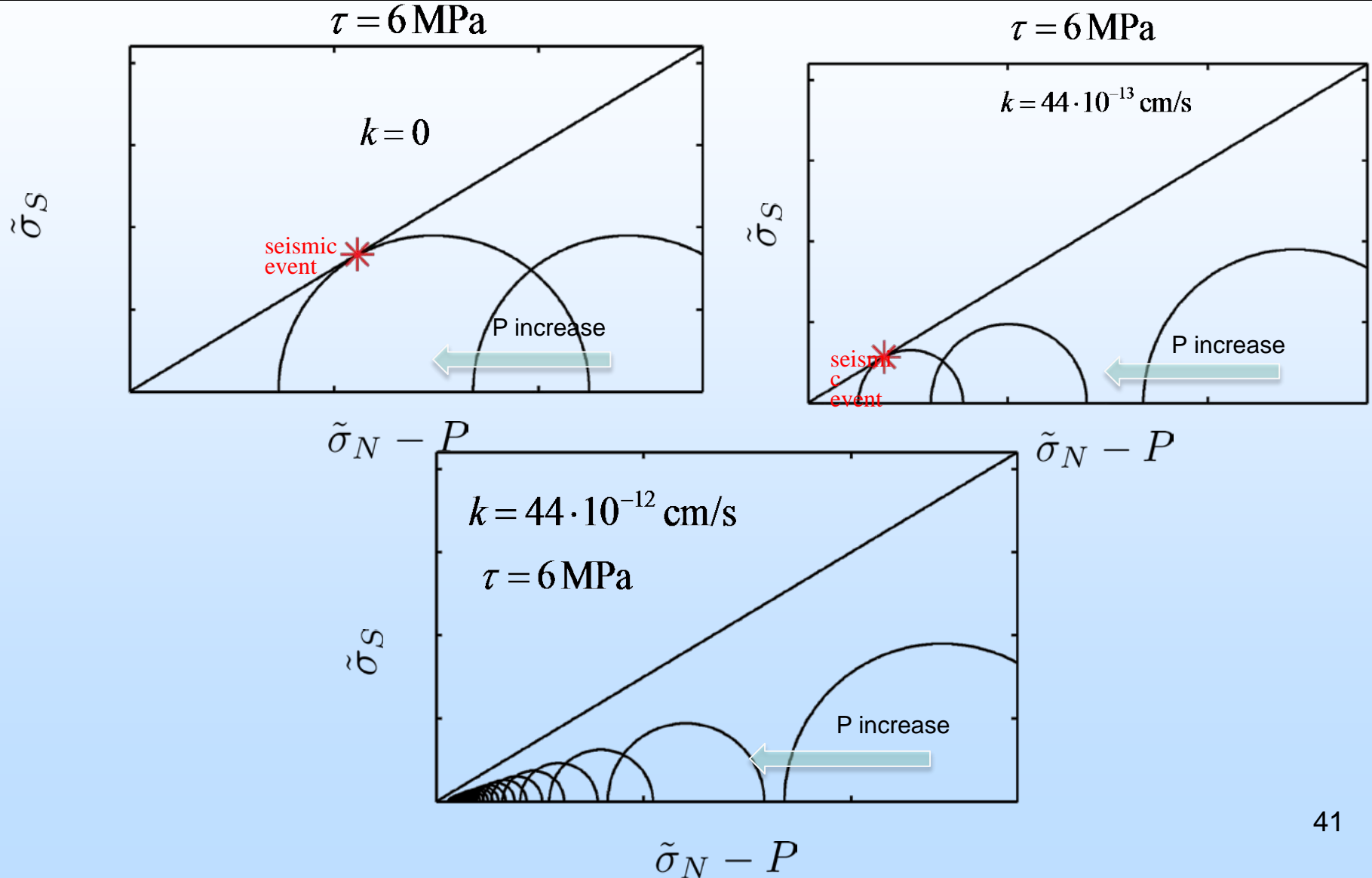


- Carbonates take more volume: Grains grow
- Larger grain-grain contact distributes load, reduces local stress
- Smaller grain-fluid contact reduces effect of pore pressure

The surface of an olivine grain (from San Carlos) after the carbonation reaction at 200°C, 1650 psi for 3 days in 0.45 ml of 1M NaHCO₃



Mineral carbonation in mafic rocks





Summary for Geomechanical modeling

- Mineral sequestration can potentially reduce seismic risk provided fluid pumping rates do not exceed a critical value
- Mineral and grain growth stores CO₂ and offsets stress loads
- Caveat: it also armors grains surfaces, fills pores and chokes off permeable pathways
 - So opening of new surfaces and permeability still requires some level of fracturing, e.g., either reaction driven or hydraulic



Accomplishments to Date

- Reaction kinetics between CO₂-bearing fluids and olivine has been investigated as a function of surface area, chemistry of CO₂-bearing fluid, fluid/olivine ratio and experimental duration (Yale U).
 - The olivine mineral fraction converted to carbonate (carbonation fraction), generally reaches an upper limit and then decreases, as conditions favorable to the formation of secondary magnesium minerals consume magnesite.
 - An empirical formula for the maximum carbonation fraction that can be achieved by reacting CO₂-bearing fluid and olivine was has been determined.
 - A reaction-rate model that fits experiments with olivine crystals, with the major species in solution, has been developed from first principles.
- A similar , but less comprehensive set of experiments has been carried out on natural basaltic rock samples collected from different volcanoes on the Big Island in Hawai'i and characterized at U Hawai'i.



Accomplishments to Date

- A new apparatus was developed for geomechanical experiments involving reactive transport and deformation (U Maryland).
 - A series of experiments involving hydrostatic compaction followed by constant strain-rate deformation was performed on thermally cracked dunite samples saturated with carbon-dioxide brines of varying composition. Permeability was monitored in situ during the experiments.
 - Comparison of the samples' volume changes to their axial strains (shortening) suggests that samples reacting with CO₂ saturated brines can accommodate more shortening, before the onset of dilation (swelling) and failure, than samples reacted with distilled water.
- Models of combined reactive flow and deformation have been developed and applied to (1) 1D geomechanical experiments, (2) mineral carbonation and induced seismicity, and (3) porosity waves involving transport of CO₂.

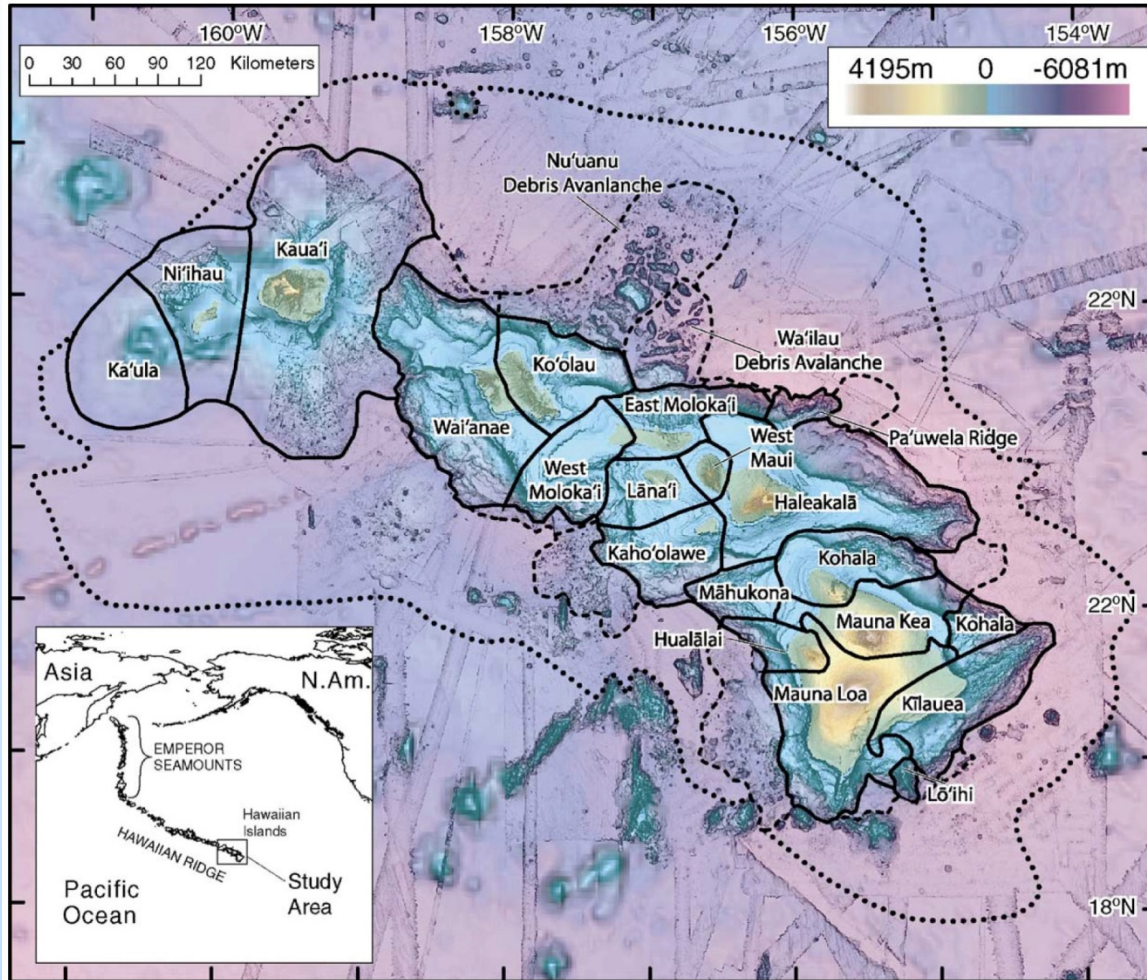


Future directions

- Finish compilation and publication of the database of thermodynamic parameters for mineral carbonation reactions (reaction-rate table).
- Finish development of multi-dimensional flow and deformation codes.
- Further geochemical experiments with natural rock samples in a new autoclave (Yale) that allows better monitoring of experimental conditions over the course of the reaction.
- Further geomechanical experiments using microtomography to image the evolution of pore space during flow and deformation.



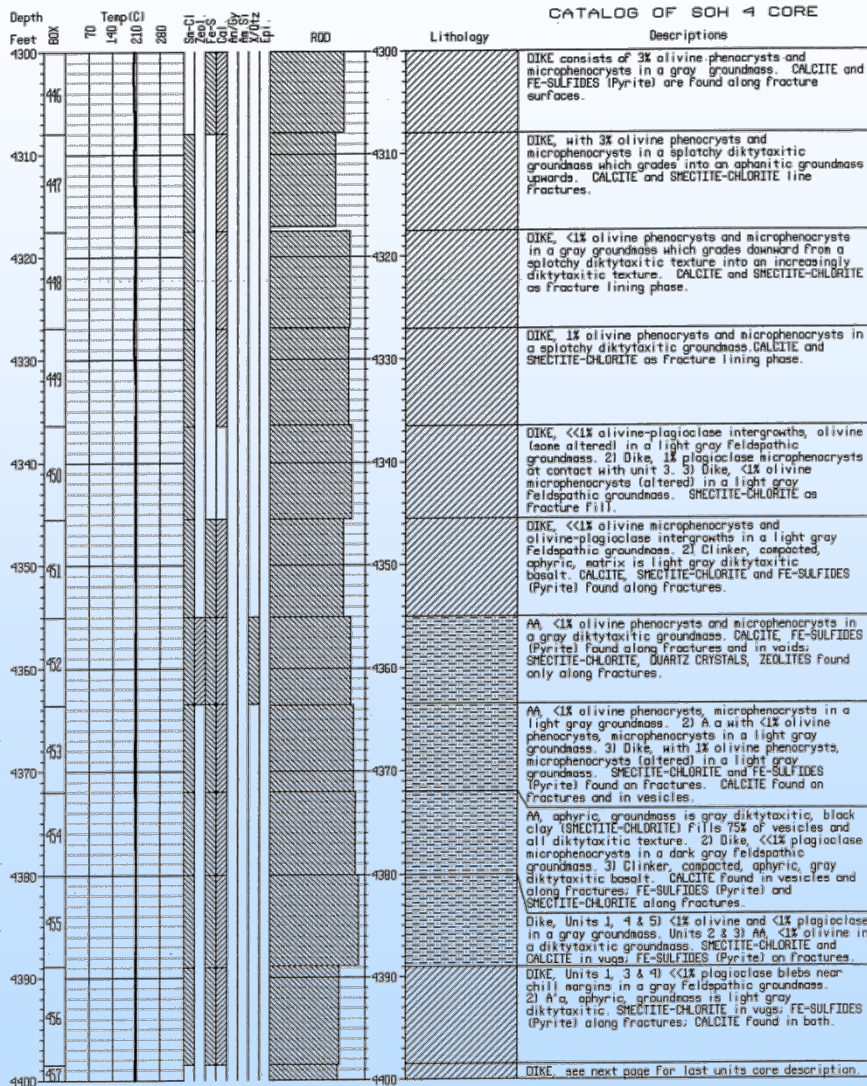
Future directions



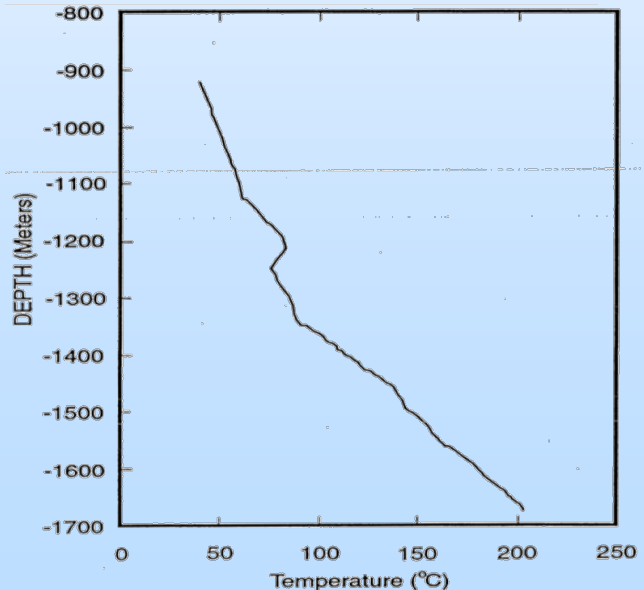
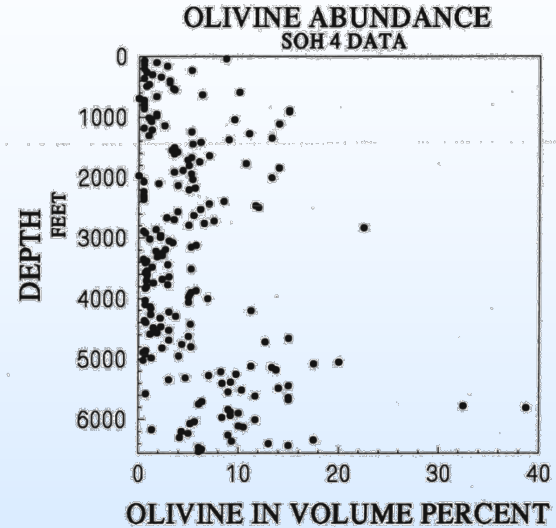
Map of combined seafloor bathymetry and subaerial topography of the shield volcanoes that make up the Hawaiian Islands. The total volume of the Hawaiian Islands volcanic edifices from base to summit and primarily olivine basalt (solid outlines), is **527,200** km³. This volume of basalt is comparable to other large igneous provinces such as the Deccan Traps in India, and is 3x the volume of the Columbia River Basalts in Washington, Idaho, and Oregon, where CO₂ injection is currently underway. *We estimate that the Hawaiian Ridge igneous province can store about 2.6×10^{17} kg CO₂, or approximately 400 times the post-industrialization anthropogenic CO₂ production (IPCC, 2007).*



Phase 2: Kilauea Scientific Observation Hole Cores (SOH)



(Figures from USGS Open-file Reports)





Appendix

1. Organization
2. Gantt chart
3. Bibliography



Organization

- There are 9 principal investigators (PIs) at 3 academic institutions:
 - 6 at Yale University,
 - 1 at University of Maryland College Park, and
 - 2 at University of Hawai'i at Mānoa.
- Yale is lead contractor, with subs to Maryland & Hawai'i
 - **Geochemical experiments** are carried out in a special high-P/T laboratory at Yale West Campus
 - **Geomechanical experiments** are carried out in a reactive flow-through apparatus at Department of Geology, U Maryland
 - **Collection and analysis of field samples** for experiments is done by through Department of Geology & Geophysics, U Hawai'i
 - **Development of theory and simulation codes** is done at Department of Geology & Geophysics, Yale U



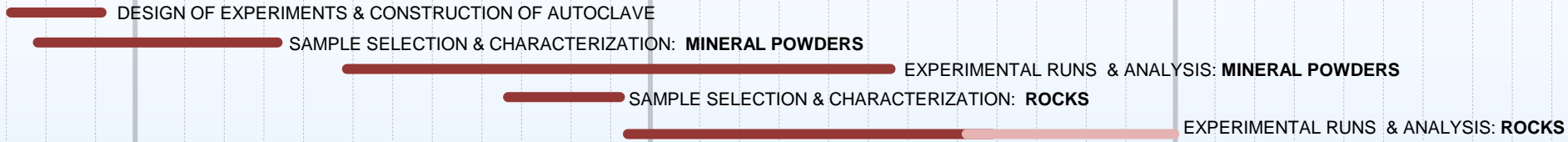
Gantt Chart

2011

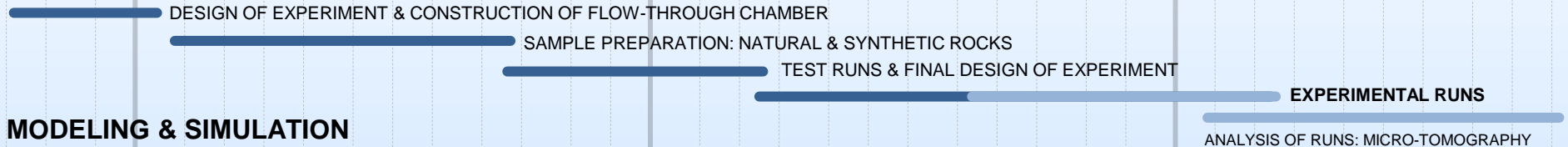
2012

2013

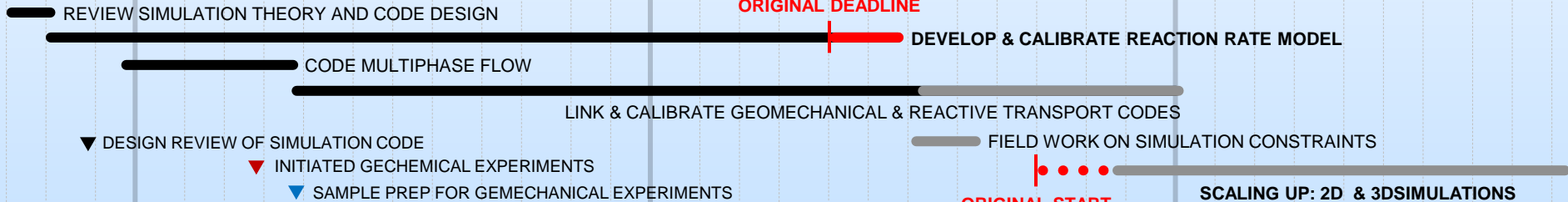
GEOCHEMICAL EXPERIMENTS



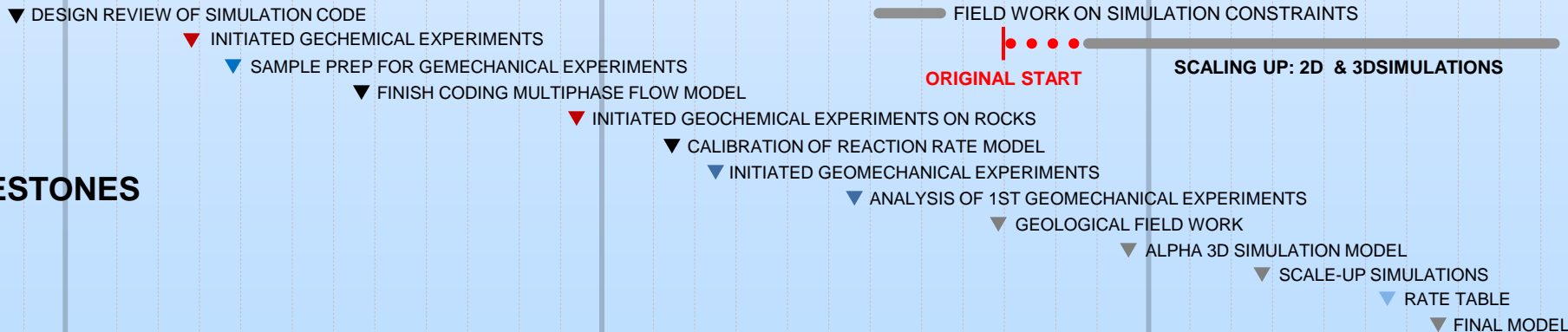
GEOMECHANICAL EXPERIMENTS



MODELING & SIMULATION



MILESTONES



10.4 11.1 12.6 1.3 2.7 3.7 4.4 5.2 6.6 7.4 8.1 9.5 10.3 11.7 12.5 1.2 2.6 3.5 4.2 5.7 6.4 7.2 8.6 9.3 10.1 11.5 12.3 1.7 2.4 3.4 4.1 5.6 6.3 7.1 8.5 9.2 9.30



Bibliography

- Three submitted manuscripts under review
 - “Mg isotope fractionation during olivine dissolution”, Lin Qiu and Zhengrong Wang, submitted to GCA.
 - “Experimental Study of the Reaction Kinetics Between CO₂-Bearing Fluid and Olivine”, Qiu et al., submitted to *Chemical Geology*.
 - “The Impact of Porosity Waves on Crustal Reaction Progress and CO₂ Mass Transfer”, Tian M and Ague J, submitted to *Earth and Planetary Science Letters*.
- Three Peer-reviewed publications published at this time
 - “Mineral Carbon Sequestration and Induced Seismicity,” Yarushina and Bercovici, *Geophysical Research Letters* **40**, 2013, 814-818, doi: 10.1002/grl.50196.
 - “Two-phase damage models of magma-fracturing”, Cai Z and Bercovici D, *Earth and Planetary Science Letters*, 368 (2013) 1–8.
 - “Rock deformation models and fluid leak-off in hydraulic fracturing”, Yarushina V, Bercovici D and Oristaglio M, *Geophysical Journal International*, accepted 2013 May 13, published online June 8, 2013
- Five manuscripts in preparation



Bibliography

- Papers presented at conferences
 - Integrated experimental and modeling studies of mineral carbonation, Workshop on Carbon Capture & Storage in Mafic and Ultramafic Rocks, January 8–10, 2011, Oman.
 - An experimental study of mineral sequestration of CO₂ by mafic/ultramafic rocks, AGU 2011, San Francisco, Global Environmental Change Poster Session GC51A, December 5–9, 2011.
 - Integrated experimental and modeling studies of mineral carbonation, USGS Workshop on Carbon Sequestration in Unconventional Reservoirs, March 28–29, 2012.
 - Experimental study of the kinetics of CO₂-sequestration by olivines and Hawaiian picrites, 22nd V.M. Goldschmidt Conference, June 24–29, Montréal, Canada