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

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U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the
Infrastructure for CO_2 Storage

August 21-23, 2012

Organizations

- Yale University: Jay Ague, David Bercovici, Edward Bolton, Shun Karato, Michael Oristaglio, and Zhengrong Wang
- University of Hawaii: Kevin Johnson, Eric Hellebrand
- University of Maryland: Wenlu 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 CO_2 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,

  [mafic rocks + H_2O + CO_2] → [carbonate rocks + 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 ±10% with consistent P/T trends Simulation code reproduces reaction products and rates from subset of laboratory experiments with maximum error of ±10%, after adjusting input parameters. Code predicts reaction rates to ±20% outside range used to adjust parameters.
Geomechanical experiments	Permeability and fracture strength measurements repeatable in experiments with fluid-rock mixtures to ±20%. Simulation code reproduces reaction products and rates from subset of laboratory experiments with maximum error of ±20%, after adjusting input parameters. Code initially predicts reaction rates to ±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
- Geochemical modeling
- Geo-mechanical experiments

Experimental setup

silicate rock carbonate rock

$$Mg_2SiO_4 + 2\,CO_2 \longrightarrow 2\,MgCO_3 + SiO_2$$

olivine pyroxene

$$2\,Mg_2SiO_4 + CaMgSi_2O_6 + 2\,CO_2 + 2\,H_2O \longrightarrow CaCO_3 + MgCO_3 + Mg_2Si_2O_5(OH)_5$$

calcite magnesite serpentine

Mineral Carbonation

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

GEOMECHANICAL Experiments & Modeling

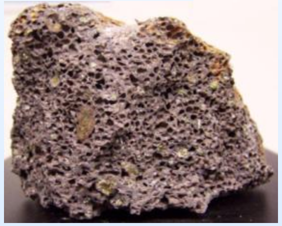
Understand the feedbacks: effects of chemical reactions on rock matrix and pore space

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

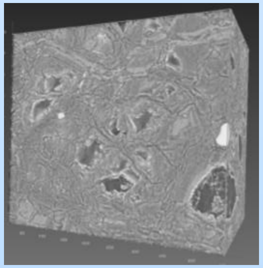
Cold seal and flow-through experiments on **rocks**

INITIAL PORE SPACE

STRESS FRACTURES
PORE SPACE ALTERATION

REACTION KINETICS

CHEMICAL
HYDROTHERMAL
& GEOMECHANICAL
PROCESSES



3D micro-tomogram *of carbonized dunite sample*

SCALE UP

Big Island, Hawai'i

MODELING & SIMULATION

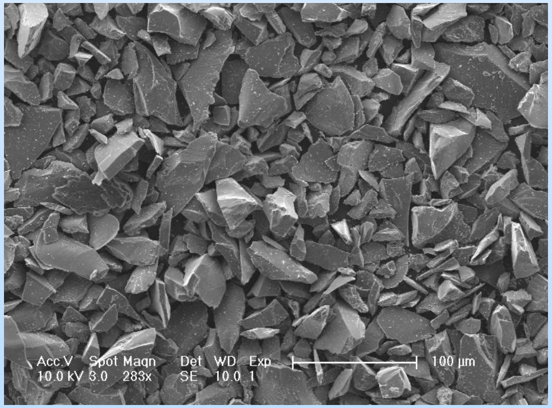
Build an integrated simulation model for geochemical & geomechanical processes

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

DESIGN

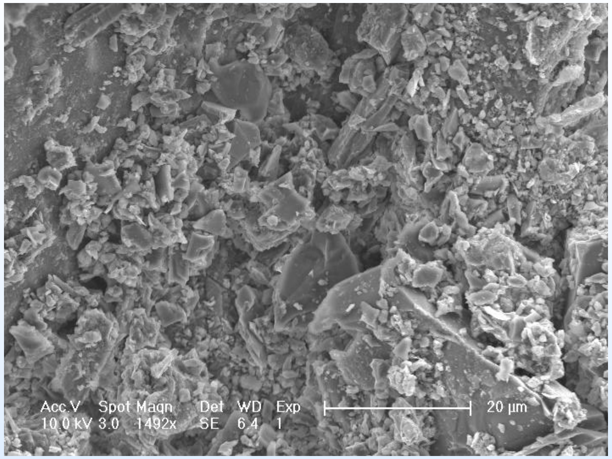
PHASE II FIELD STUDY

Geochemical experiments

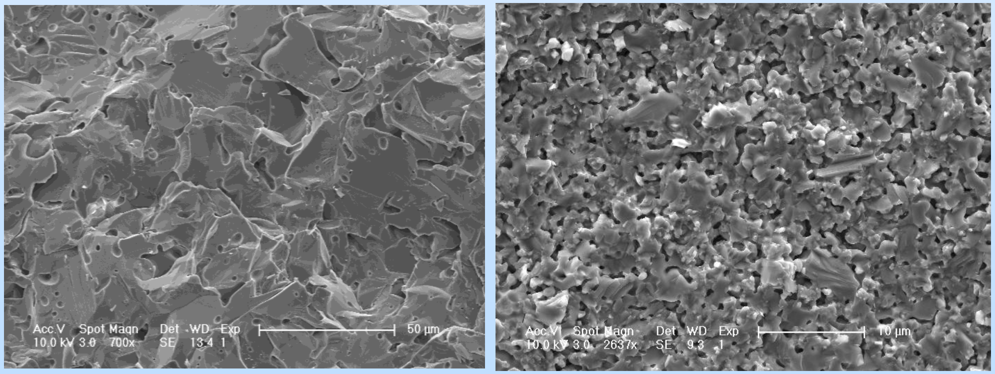


Samples

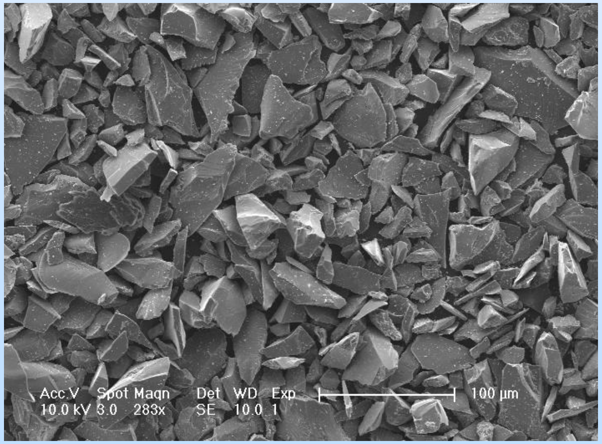
Gem-quality single crystals (left: Olivine, Right: Garnet)



Basalt powder



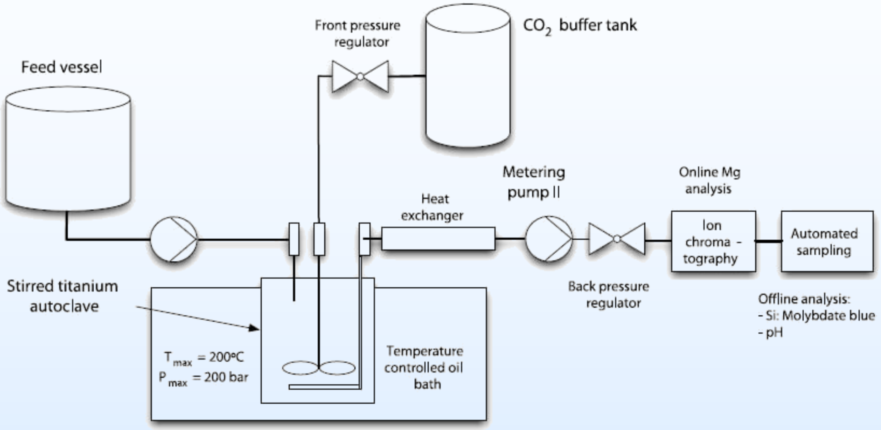
Sintered olivine and basalts



Olivine powder

Goal for geochemical experiments

- Provide direct constraints on carbonation efficiency, at various conditions
- Understand physical and chemical processes that help to scale up chemical reactions involving minerals to mineral aggregates and rocks
- Calibrating our numerical models



Flow-through reaction cells

A significant amount of experiments were conducted in a closed system to understand the reaction rate variation as system approaches to chemical equilibrium

LUX ET VERITAS

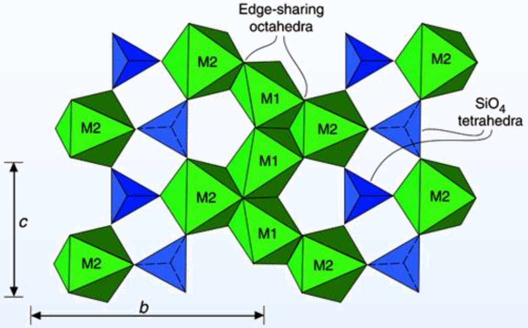
YALE UNIVERSITY GEOLOGY AND GEOPHYSICS

Rates and Mechanisms of Olivine Carbonation

Two-step olivine carbonation process

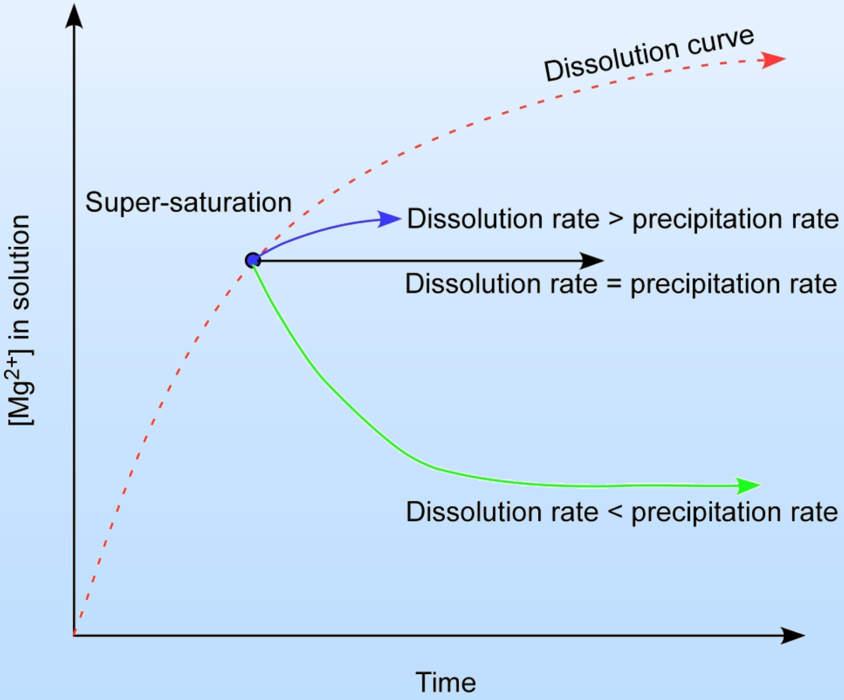
$$(Mg_{0.9}, Fe_{0.1})_2SiO_4 + 4H^+ \rightarrow 1.8Mg^{2+} + 0.2Fe^{2+} + H_4SiO_4$$

$$(Mg_{0.9}, Fe_{0.1})_2SiO_4 + 4OH^- \underset{?}{\rightarrow} 1.8Mg(OH)_2 + 0.2Fe(OH)_2 + H_4SiO_4$$



$$Mg^{2+} + CO_3^{2-} = MgCO_3 \downarrow$$

Rate of carbonation ≈ dissolution only when Dissolution rate <= precipitation rate



Geochemical experiments

Dissolution reaction

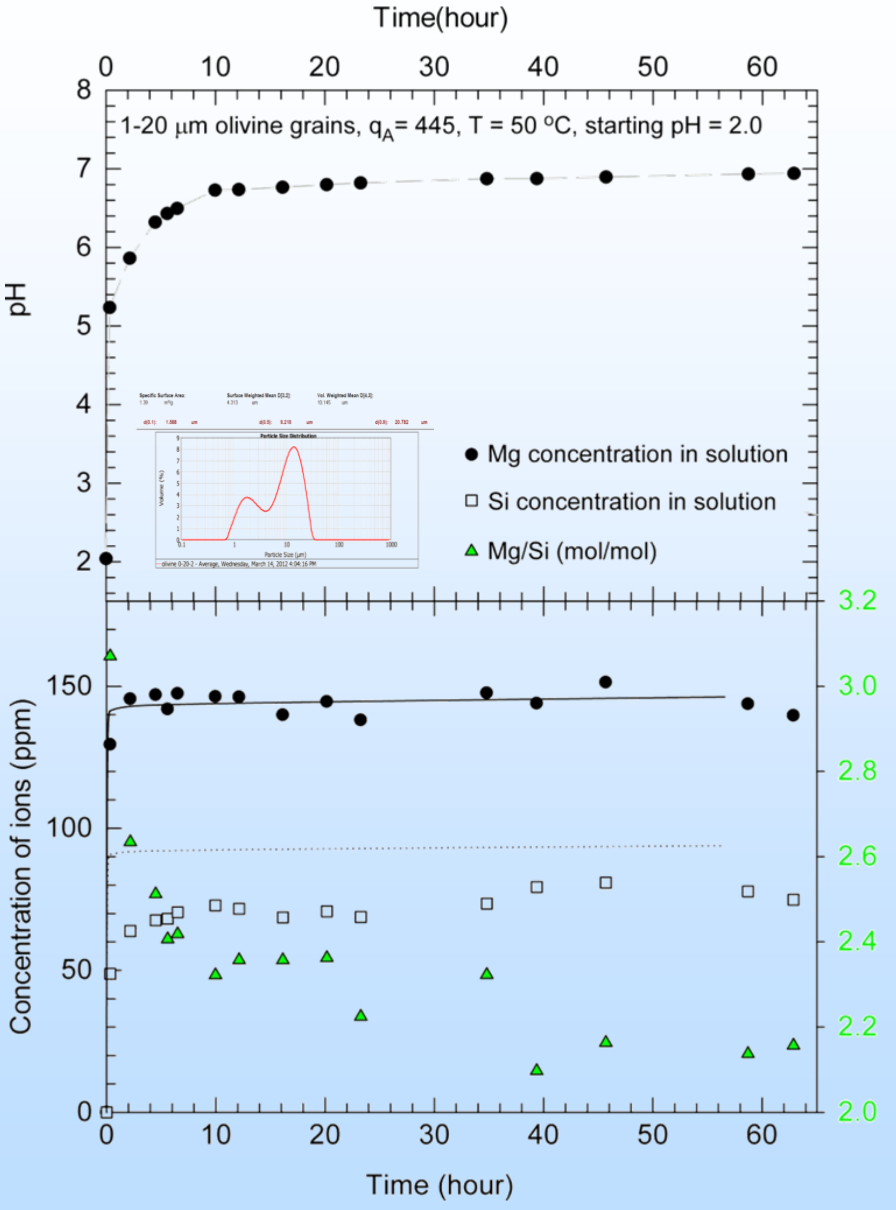
Dissolution

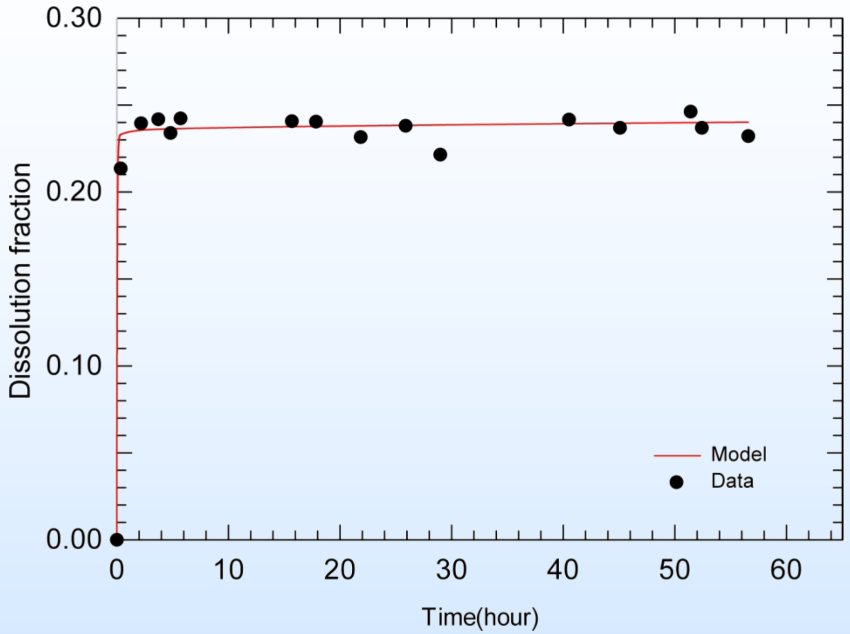
Time	Temperature C	PH	Olivine 10-20μm	Basalt 5-10μm	Basalt 10-40μm	Basalt 100μm
1 day	200	2		✓		✓
	200	4.0	✓		✓	
	200	7.0	✓		✓	
	200	8		✓		✓
	200	9.3	✓		✓	
3 days	200	2		✓		✓
	200	4.0	✓		✓	
	200	7.0	✓		✓	
	200	8		✓		✓
	200	9.3	✓		✓	
5 days	200	2				
	200	4.0	✓		✓	
	200	7.0	✓		✓	
	200	8				
	200	9.3	✓		✓	
7 days	200	2		✓		✓
	200	4.0	✓		✓	
	200	7.0	✓		✓	
	200	8		✓		✓
	200	9.3	✓		✓	
14 days	200	2		✓		✓
	200	4.0	✓		✓	
	200	7.0	✓		✓	
	200	8		✓		✓
	200	9.3	✓		✓	

Olivine dissolution (short time interval)

hours	Tem C	PH	0–30μm
0.3	50	2 and 10	✓
2.2	50	2 and 10	✓
4.5	50	2 and 10	✓
5.6	50	2 and 10	✓
6.5	50	2 and 10	✓
10.0	50	2 and 10	✓
12.1	50	2 and 10	✓
16.1	50	2 and 10	✓
20.2	50	2 and 10	✓
23.3	50	2 and 10	✓
34.8	50	2 and 10	✓
39.4	50	2 and 10	✓
45.7	50	2 and 10	✓
58.7	50	2 and 10	✓
62.9	50	2 and 10	✓
hours	Tem C	PH	Grain
1	100	2 and 10	✓
2	100	2 and 10	✓
3	100	2 and 10	✓
5	100	2 and 10	✓
7	100	2 and 10	✓
9	100	2 and 10	✓
25	100	2 and 10	✓
48	100	2 and 10	✓
hours	Tem C	PH	0-30 μm
3	100	2 and 10	✓
6	100	2 and 10	✓
9	100	2 and 10	✓
26	100	2 and 10	✓
hours	Tem C	PH	0-30 μm
0.3	200	2 and 10	✓
0.7	200	2 and 10	✓
2.0	200	2 and 10	✓
4.0	200	2 and 10	✓
6.0	200	2 and 10	✓
8.0	200	2 and 10	✓
18.0	200	2 and 10	✓
24.0	200	2 and 10	✓

Dissolution of olivine in closed systems

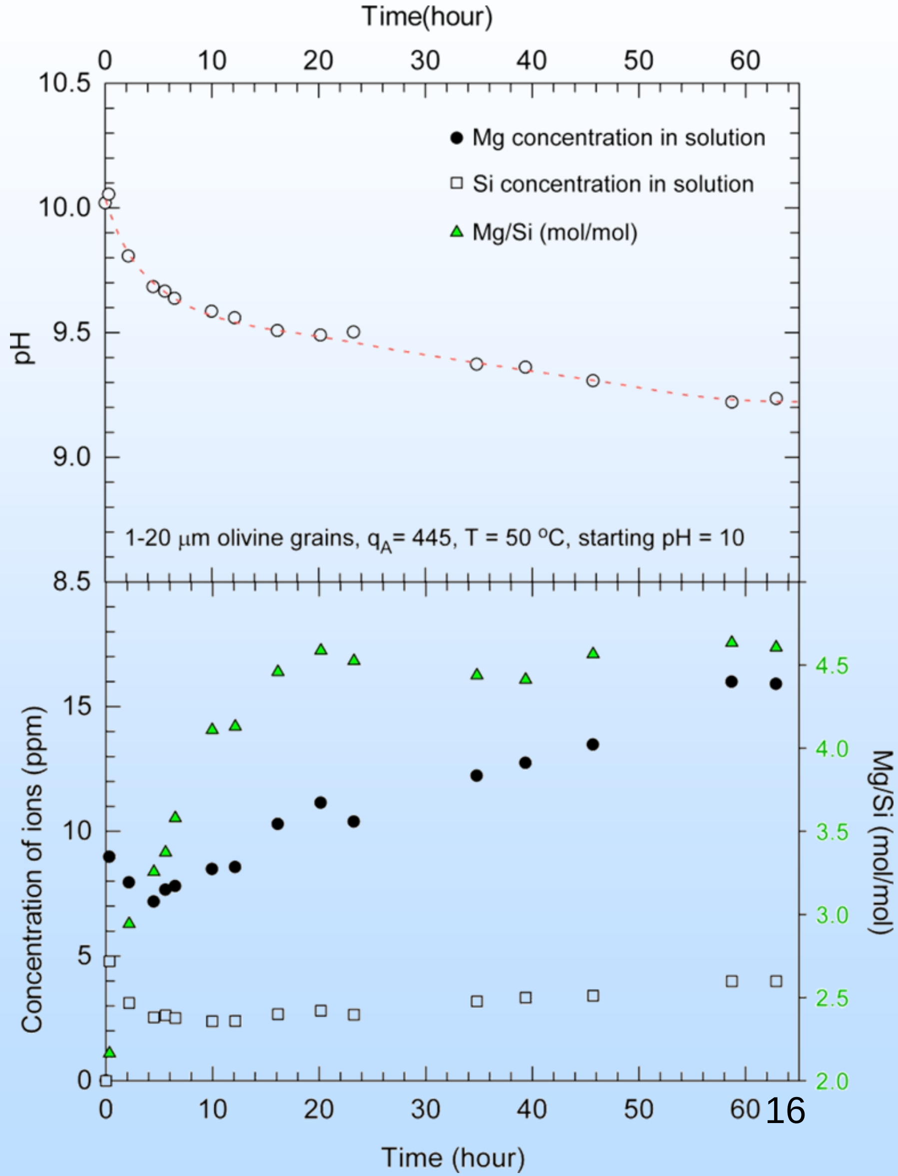




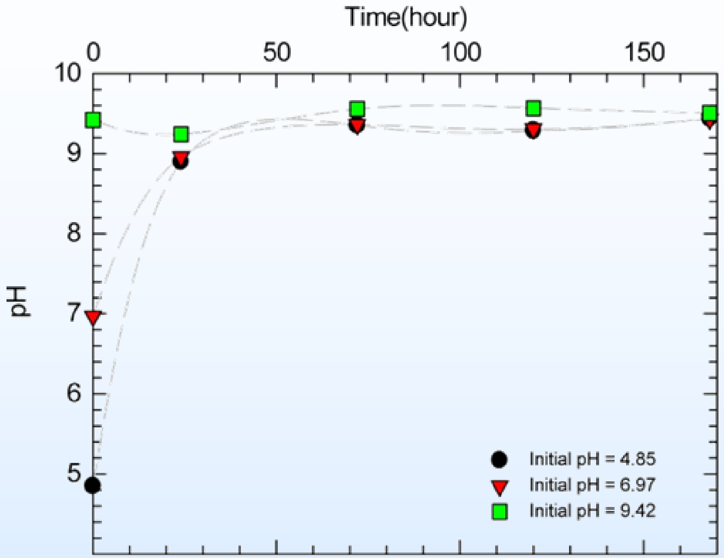
Precipitation of SiO_2

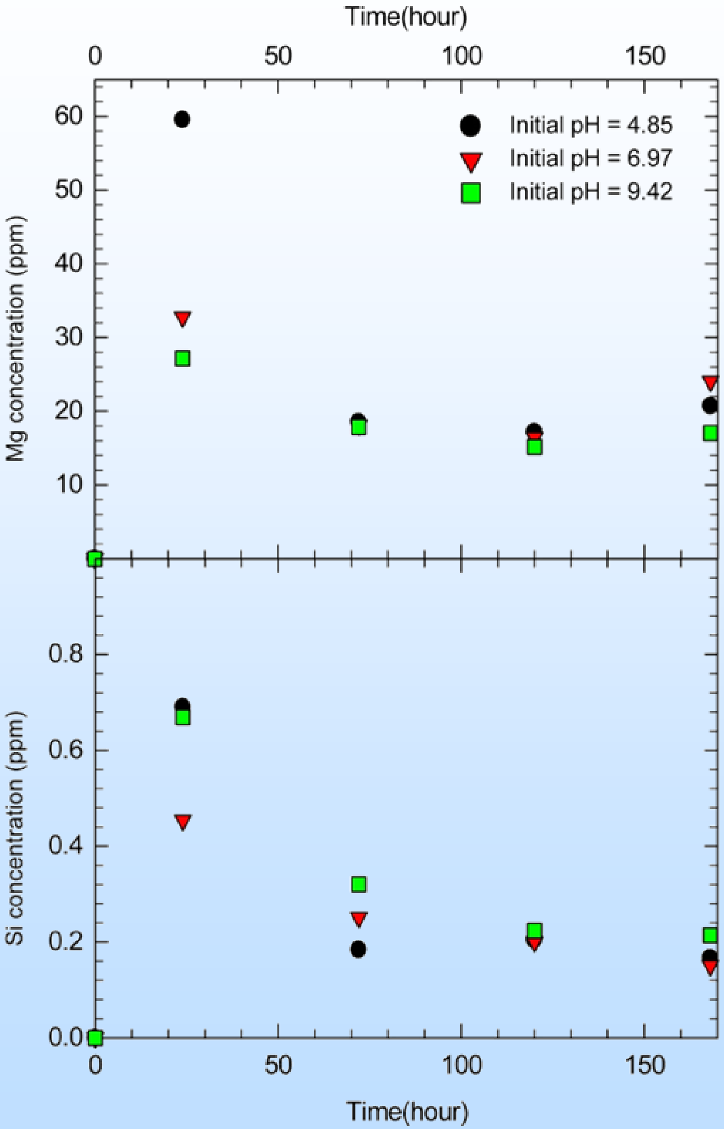
Dissolution of olivines in closed systems

Precipitation of hydrous Mg-silicates during dissolution



Dissolution of olivine at 200^{o}C, 150 bar





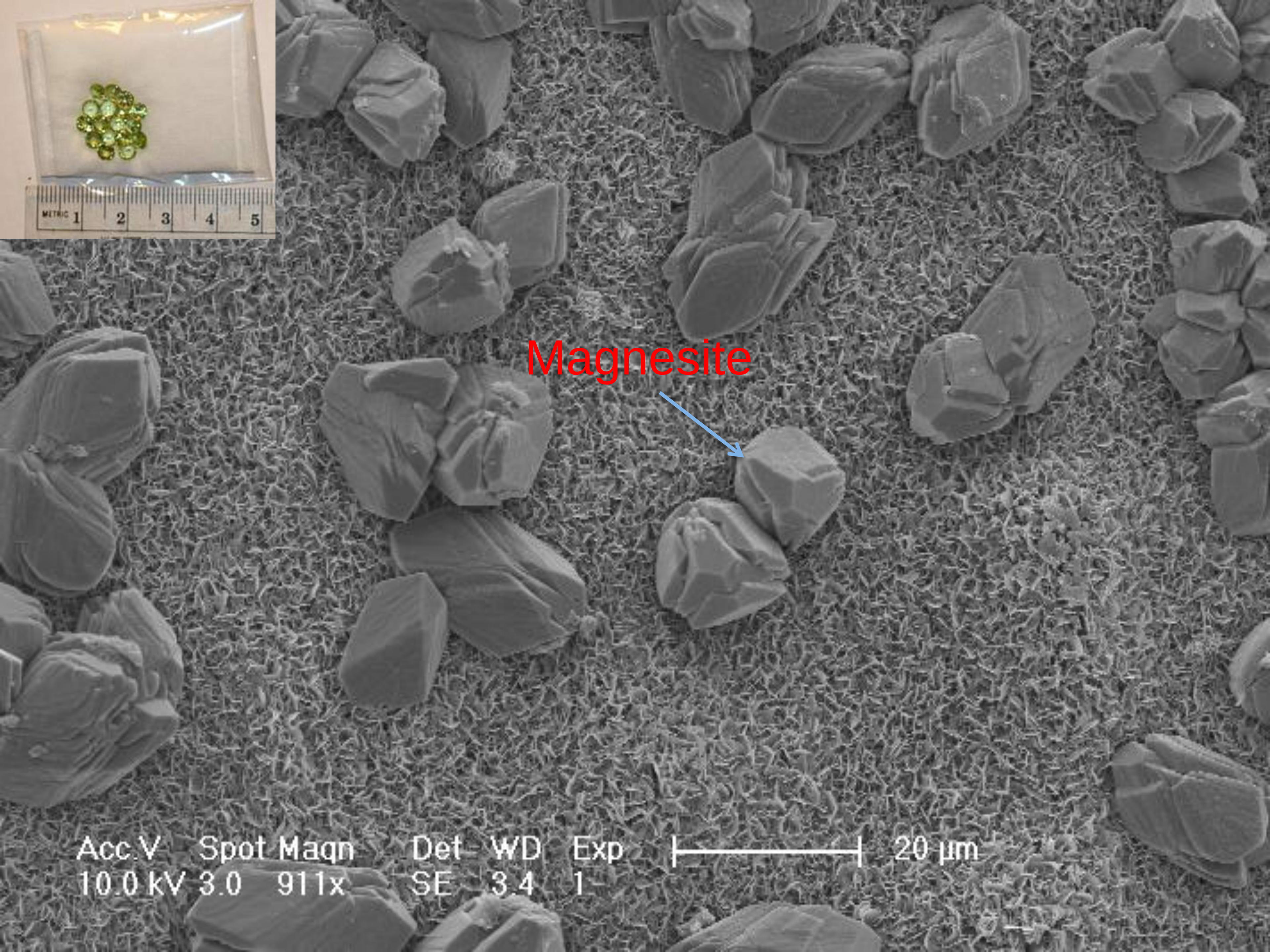
Precipitation of significant amount of hydrous Mg-silicates

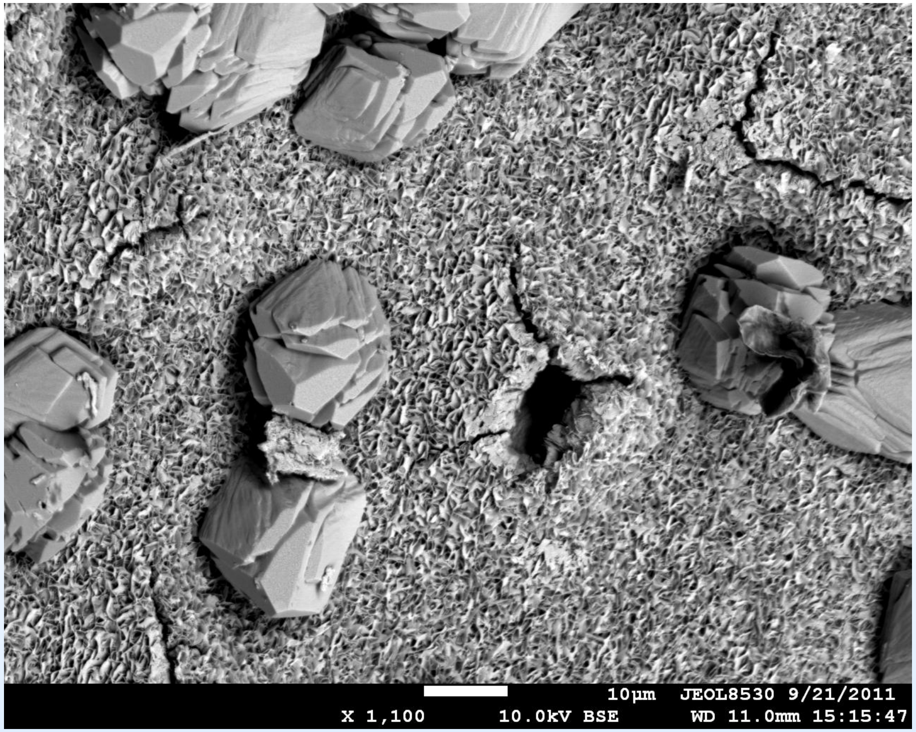
Geochemical experiments

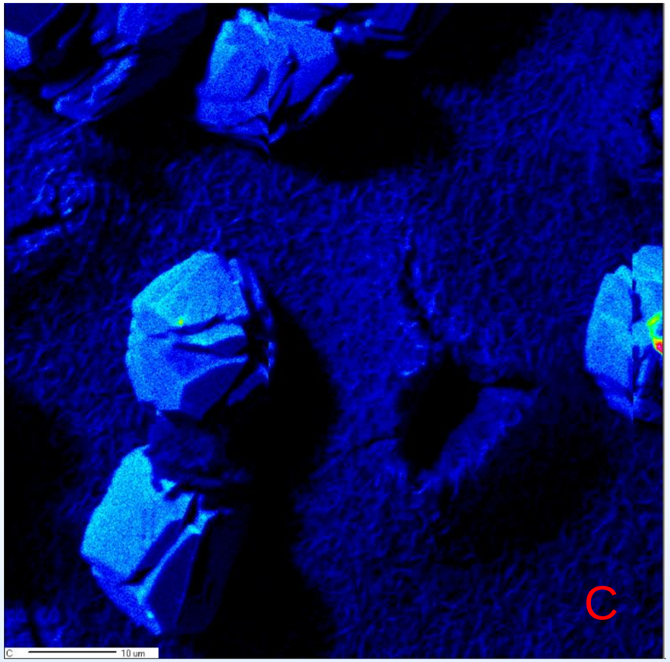
Carbonation reaction, 200^{o}C, 150 bar

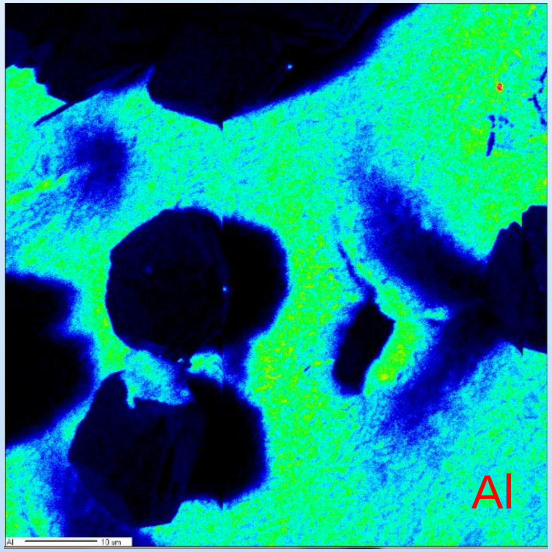
Carbonation

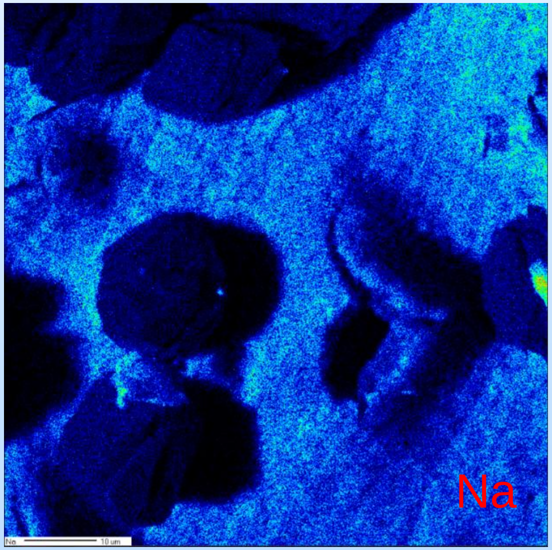
		Olivine			Basalt			
Days		Grain	1-5µm	10-20µm	1-5µm	5-10µm	10-40µm	100µm
1	1N NaHCO3	✓		✓		✓	✓	✓
	3N NaHCO3	✓				✓	✓	✓
3	1N NaHCO3	✓	✓	✓	✓	✓	✓	✓
	3N NaHCO3	✓	✓	✓	✓	✓	✓	✓
5	1N NaHCO3	✓					✓	
	3N NaHCO3						✓	
7	1N NaHCO3	✓		✓		✓	✓	✓
	3N NaHCO3	✓		✓		✓	✓	✓
14	1N NaHCO3					✓		✓
	3N NaHCO3					✓		✓

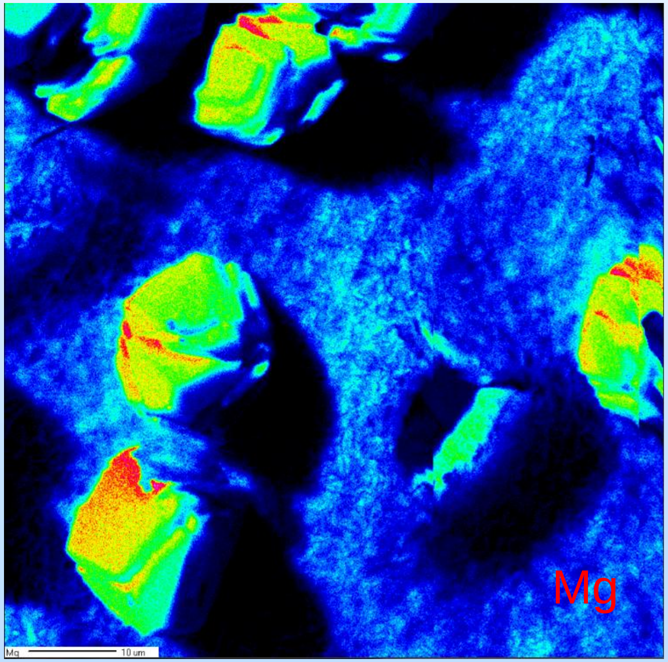

METRIC 1 2 3 4 5
Magnesite
Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 911x SE 3.4 1
20 µm

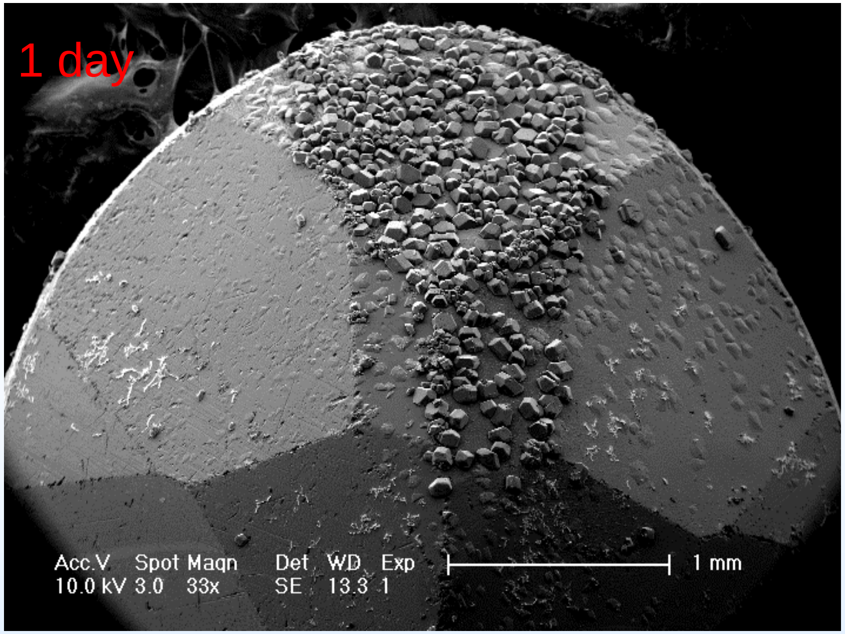

10µm JEOL8530 9/21/2011
X 1,100 10.0kV BSE WD 11.0mm 15:15:47

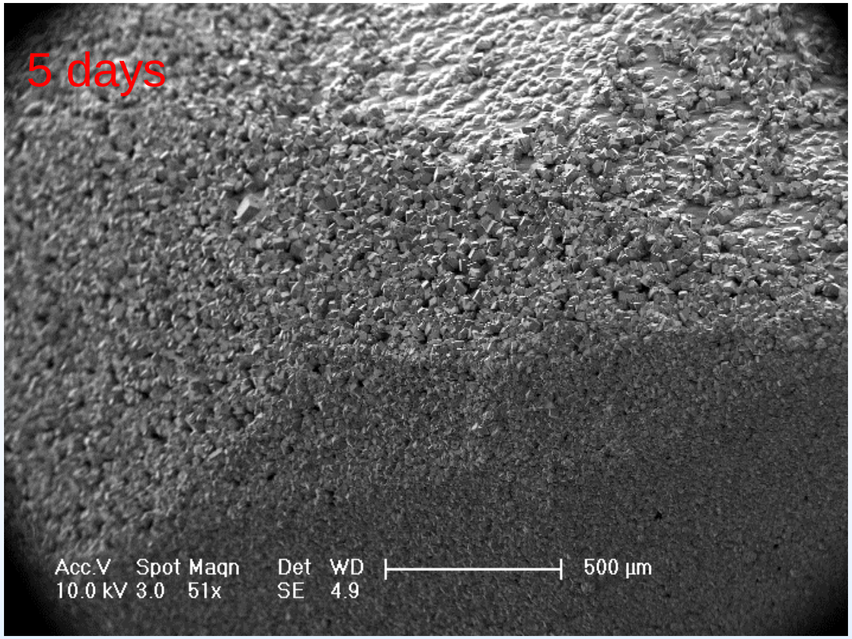

C
C
10 um

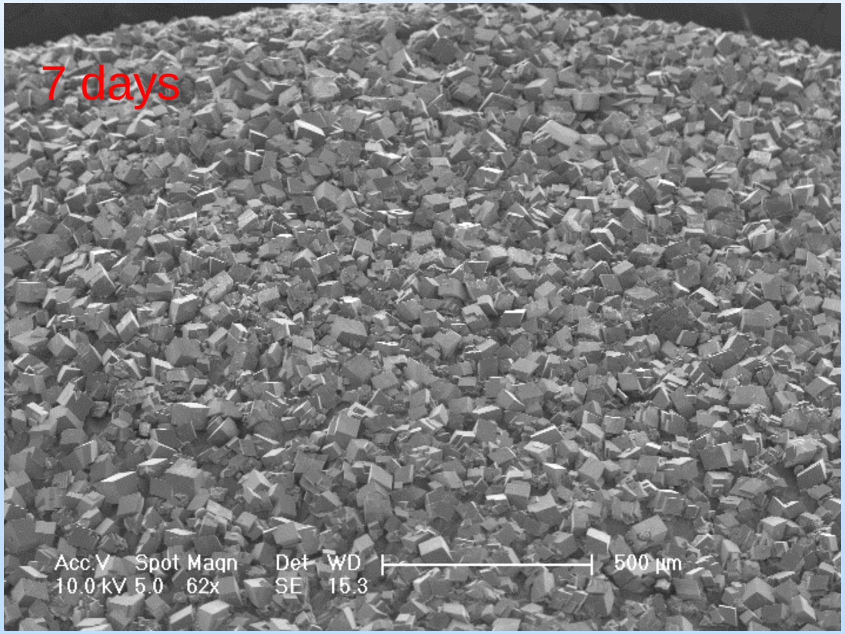

Al
Al
10 um

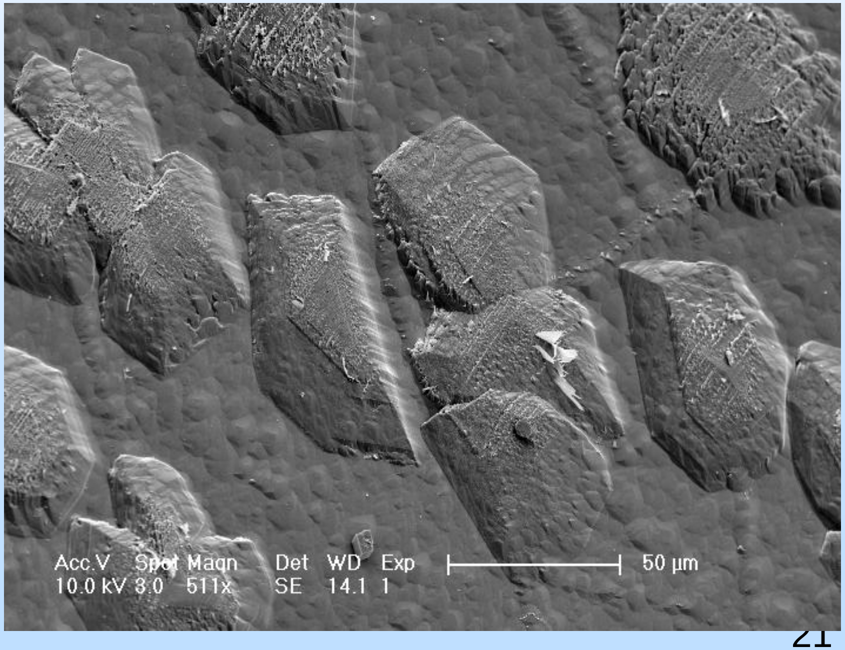

Na
Na
10 um


Mg
Mg
10 um

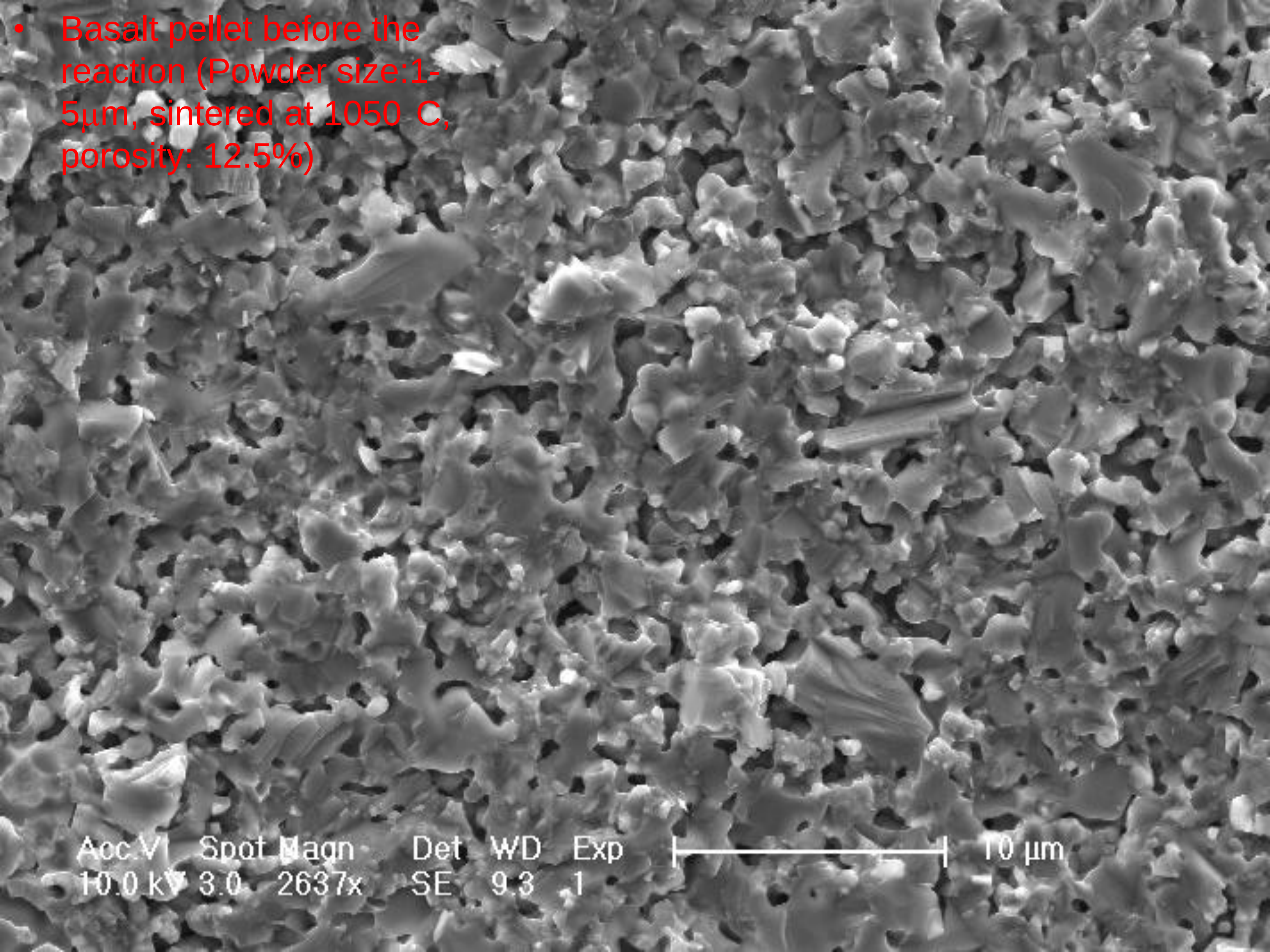

1 day
Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 33x SE 13.3 1
1 mm


5 days
Acc.V Spot Magn Det WD
10.0 kV 3.0 51x SE 4.9
500 µm

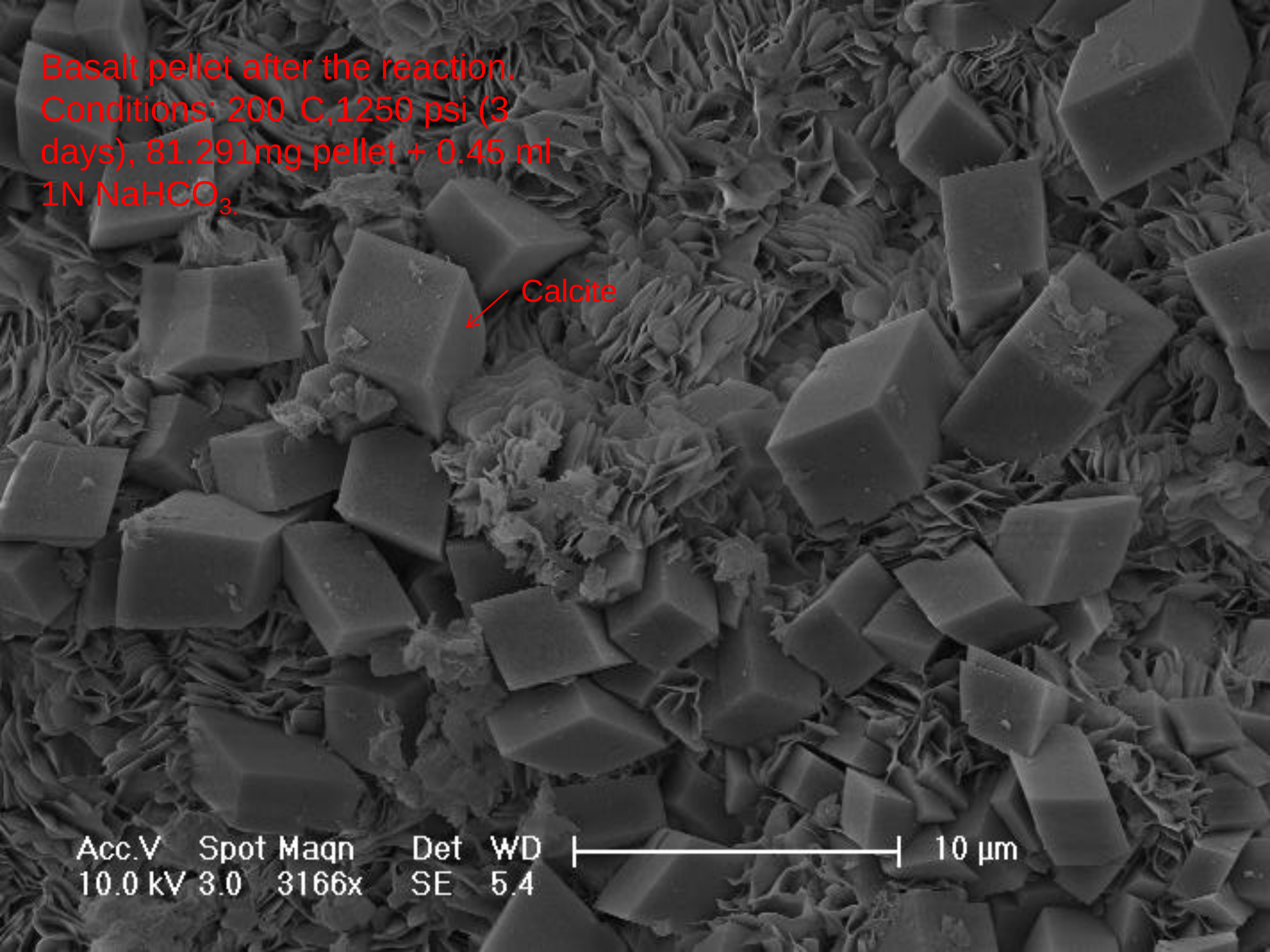

7 days
Acc.V Spot Magn Det WD
10.0 kV 5.0 62x SE 15.3
500 µm

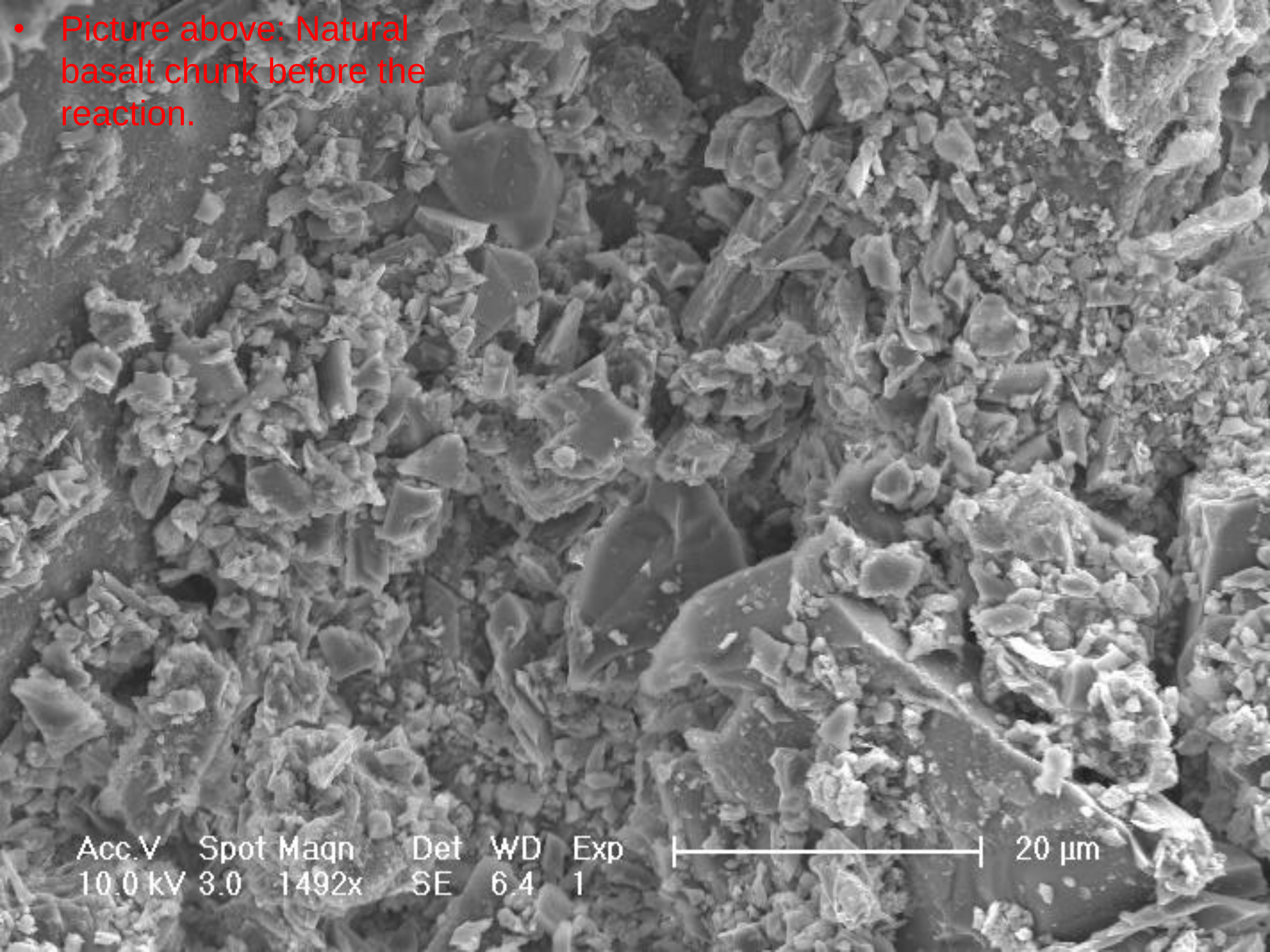

Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 511x SE 14.1 1
50 µm

- Basalt pellet before the reaction (Powder size:1-5μm, sintered at 1050 C, porosity: 12.5%)



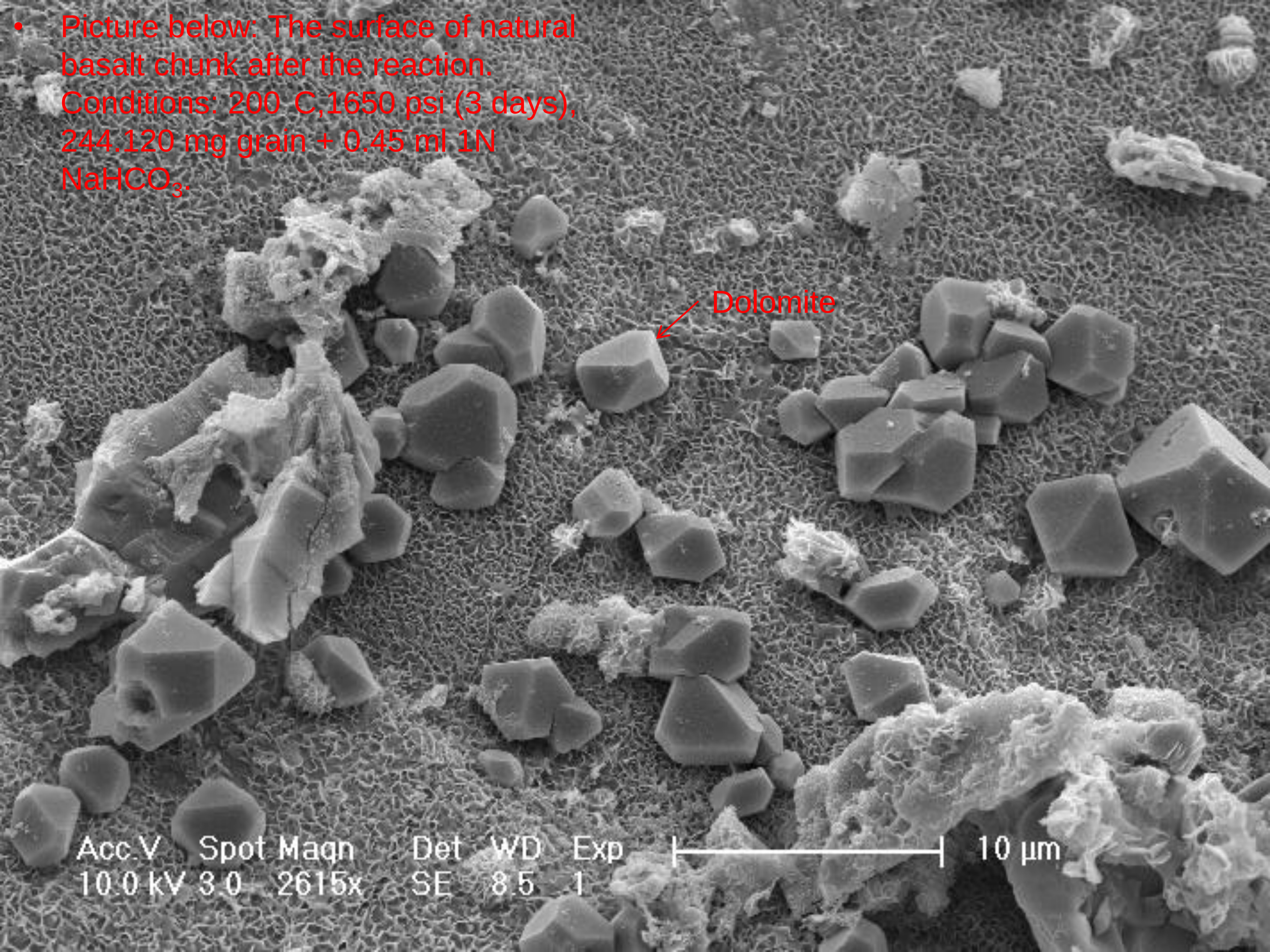
Basalt pellet after the reaction. Conditions: 200 C,1250 psi (3 days), 81.291mg pellet + 0.45 ml 1N $NaHCO_3$.





- Picture above: Natural basalt chunk before the reaction.

- 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 $NaHCO_3$.

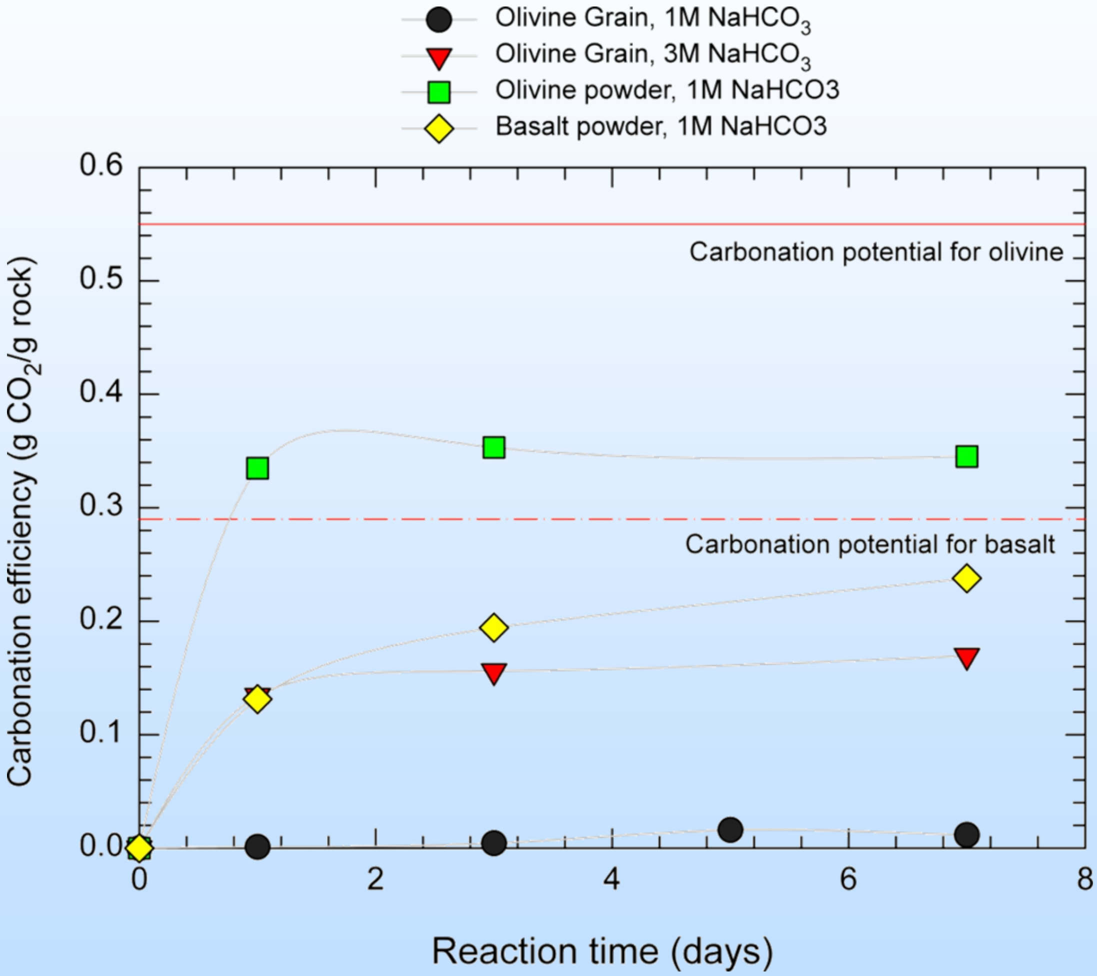


Carbonation efficiency

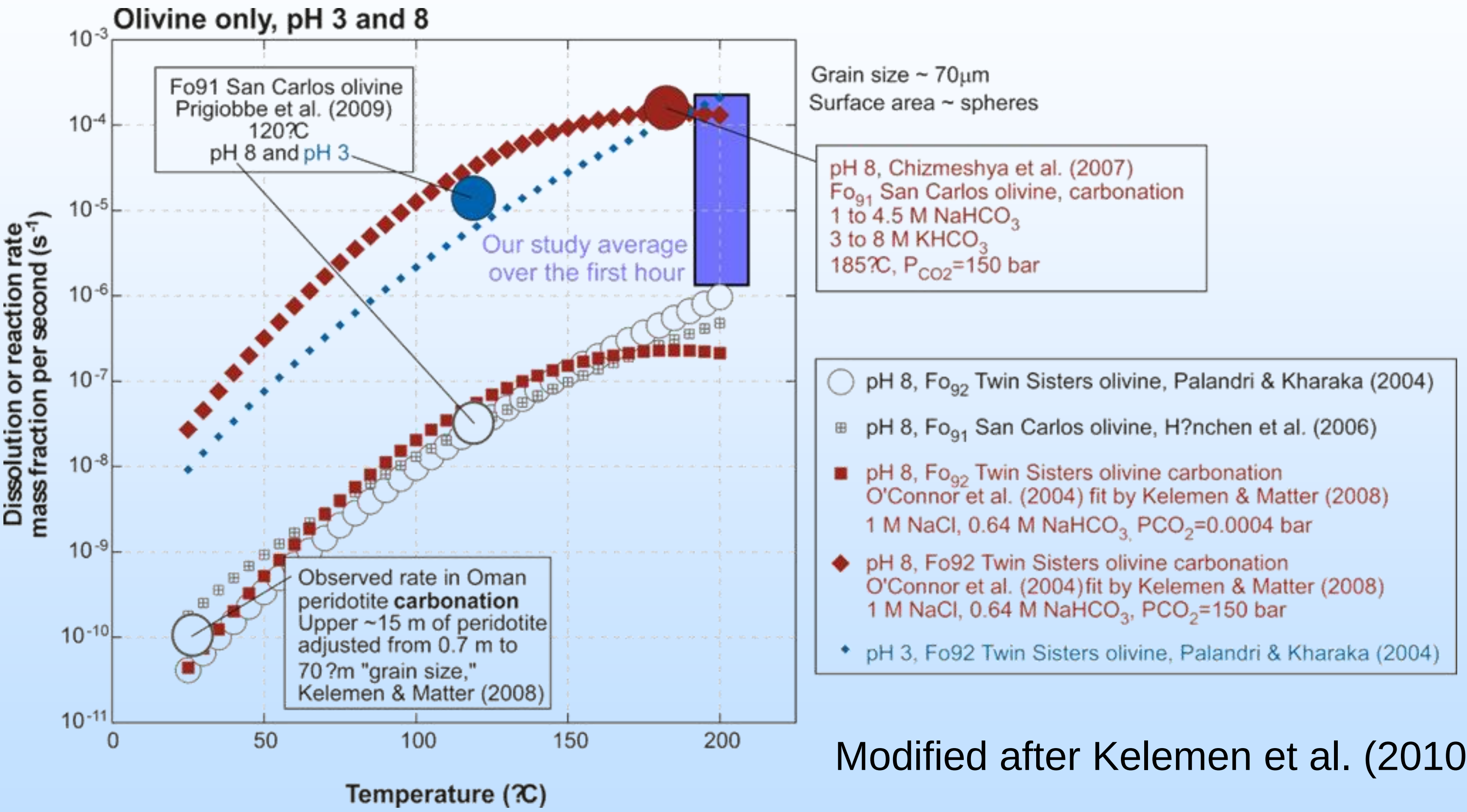
Carbonation reaction, 200^{o}C, 150 bar

1.Carbonation efficiency is a function of time, grain size, DIC content, and mineralogy

2. As reaction proceeds, carbonation rate becomes slower (Armoring effect)



Carbonation rate



Fo91 San Carlos olivine
Prigiobbe et al. (2009)
120?C
pH 8 and pH 3

Grain size ~ 70μm
Surface area ~ spheres

pH 8, Chizmeshya et al. (2007)
Fo_{91} San Carlos olivine, carbonation
1 to 4.5 M $NaHCO_3$
3 to 8 M $KHCO_3$
185?C, P_{CO2}=150 bar

Observed rate in Oman
peridotite **carbonation**
Upper ~15 m of peridotite
adjusted from 0.7 m to
70?m "grain size,"
Kelemen & Matter (2008)

- ○ pH 8, Fo_{92} Twin Sisters olivine, Palandri & Kharaka (2004)
- ⊞ pH 8, Fo_{91} San Carlos olivine, H?nchen et al. (2006)
- ■ pH 8, Fo_{92} Twin Sisters olivine carbonation
  O'Connor et al. (2004) fit by Kelemen & Matter (2008)
  1 M NaCl, 0.64 M $NaHCO_3$, PCO_2=0.0004 bar
- ◆ pH 8, Fo92 Twin Sisters olivine carbonation
  O'Connor et al. (2004) fit by Kelemen & Matter (2008)
  1 M NaCl, 0.64 M $NaHCO_3$, PCO_2=150 bar
- • pH 3, Fo92 Twin Sisters olivine, Palandri & Kharaka (2004)

Modified after Kelemen et al. (2010)

Geochemical modeling

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

MAIN FEATURES:

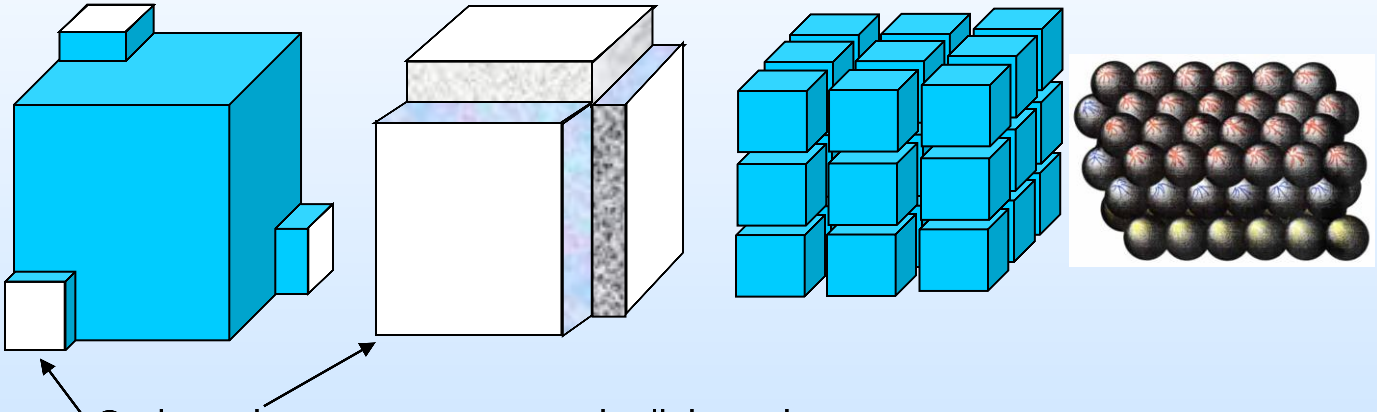
- **Aqueous and vapor phase non-isothermal flow and transport**
- **Mineral** dissolutions and precipitation via experimental **kinetics**
- **48 Minerals** covering major rock types and secondary minerals
- **30 Speciation** reactions in solution in **equilibrium** via EQ3/6, from 0-300°C
- **70** Aqueous Species
- **Fe^{3+}/Fe^{2+} Redox** reactions
- **Partitioning** between vapor and aqueous phases (O_2, CO_2, H_2O, …)
- **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

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

Grain models



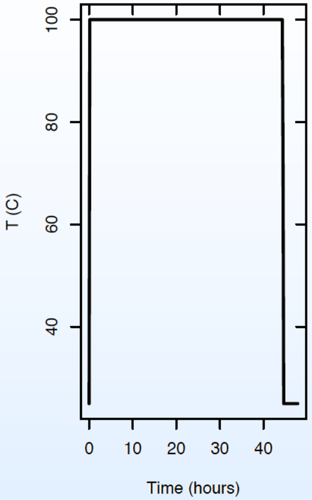
Grain-grain contact areas are the light end caps

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

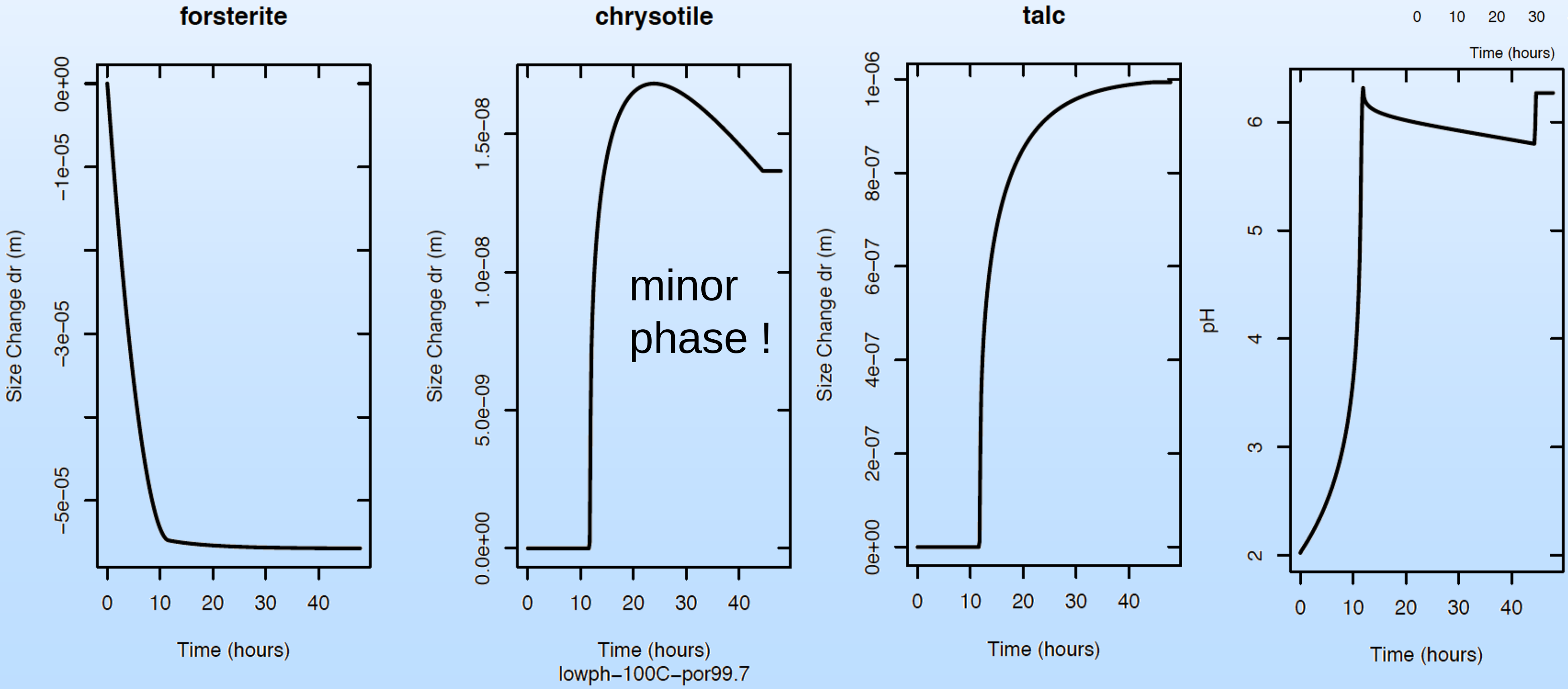
Geochemical modeling-0th order

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



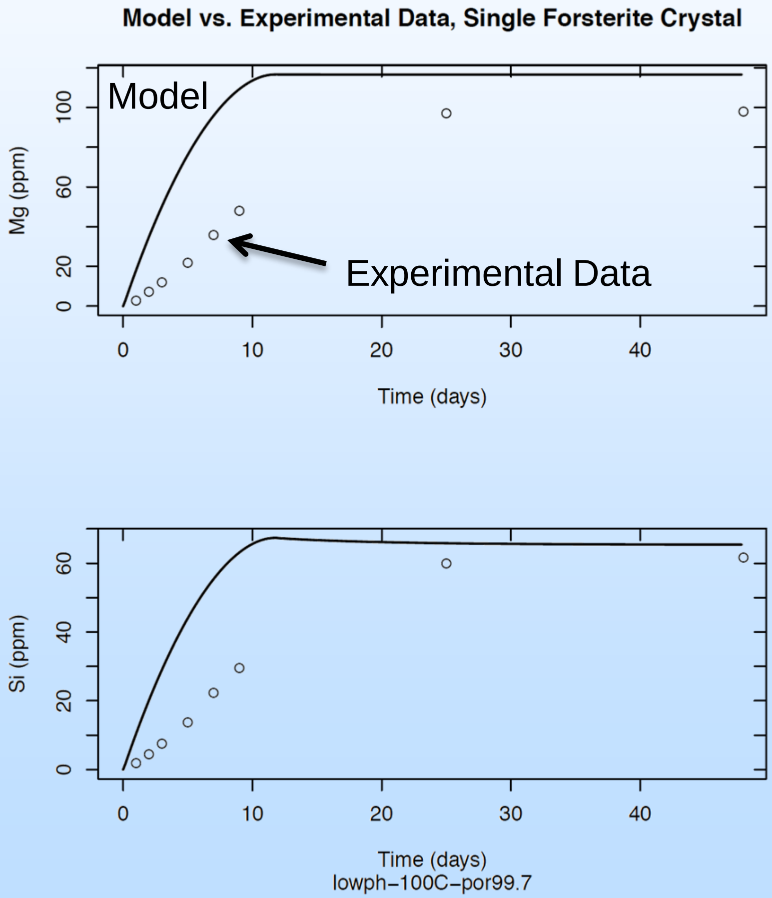
minor phase !

Geochemical modeling-0th order

- Full model with Palandri and Kharaka (2004) rates
- Forsterite single crystal dissolution at 100 C

Inverse model yields kinetic rates ~ 0.25 times those of Palandri and Kharaka (2004)

Using modified kinetics: Full model

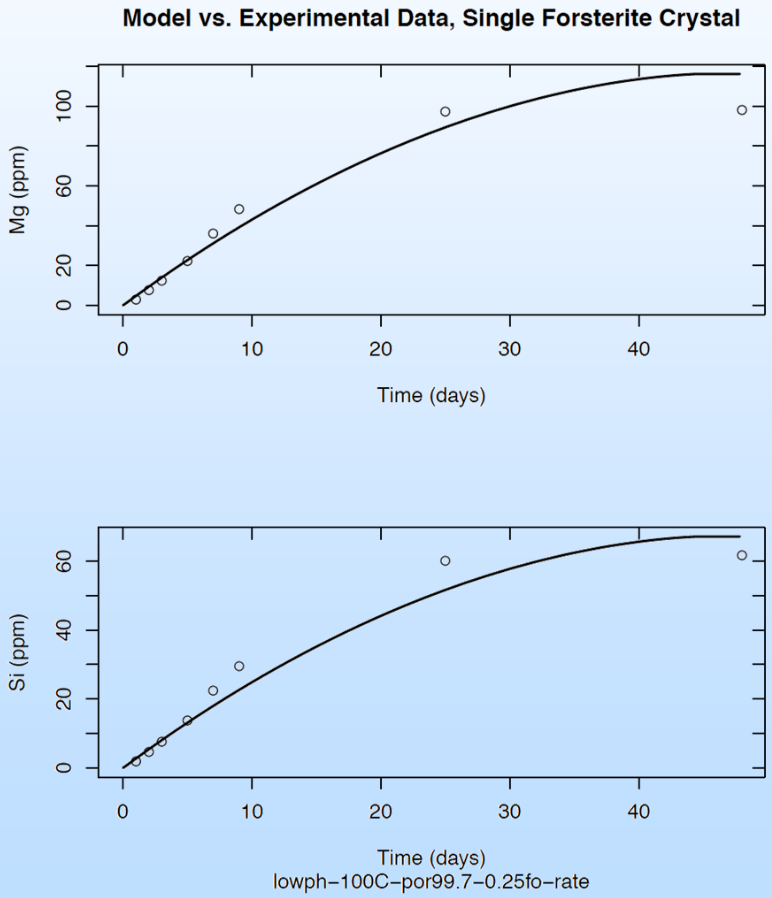


Model vs. Experimental Data, Single Forsterite Crystal

Model

Experimental Data

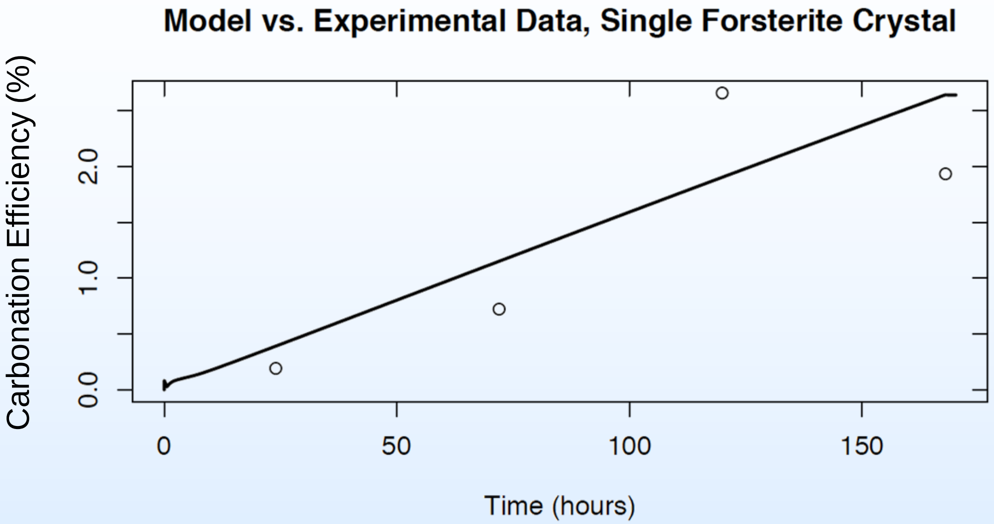
lowph−100C−por99.7

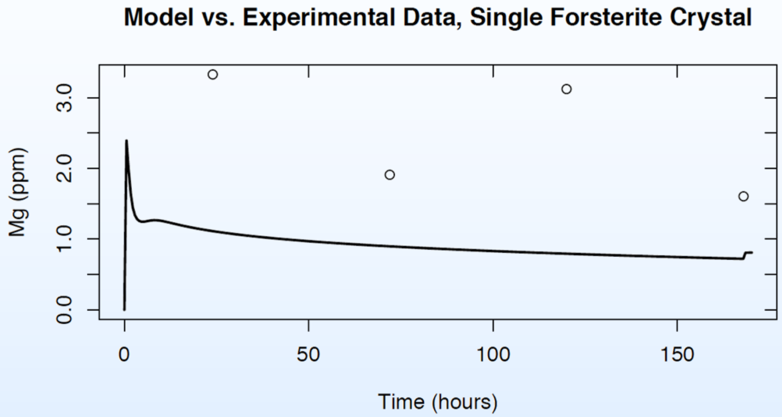


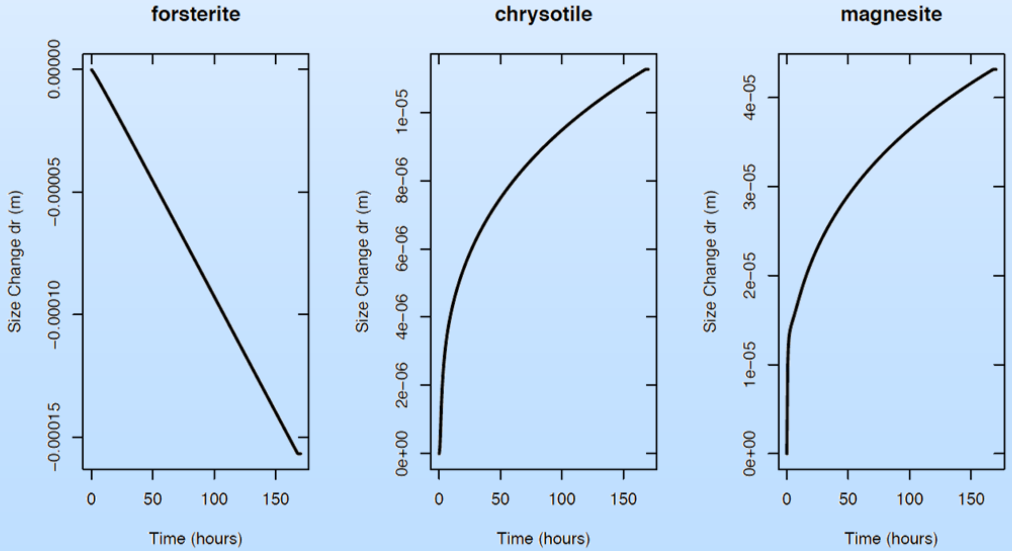
Model vs. Experimental Data, Single Forsterite Crystal

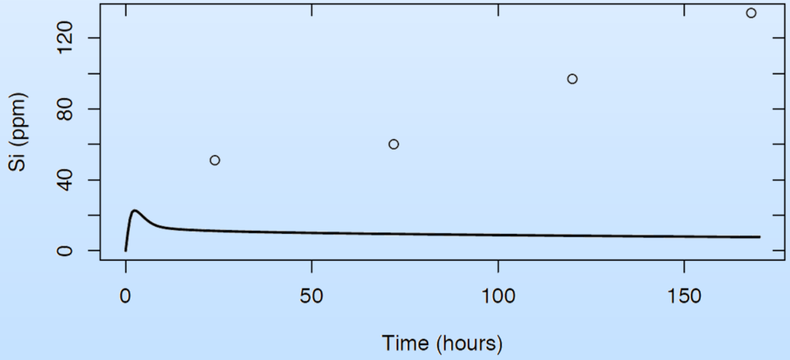
lowph−100C−por99.7−0.25fo−rate

Geochemical modeling-0th order

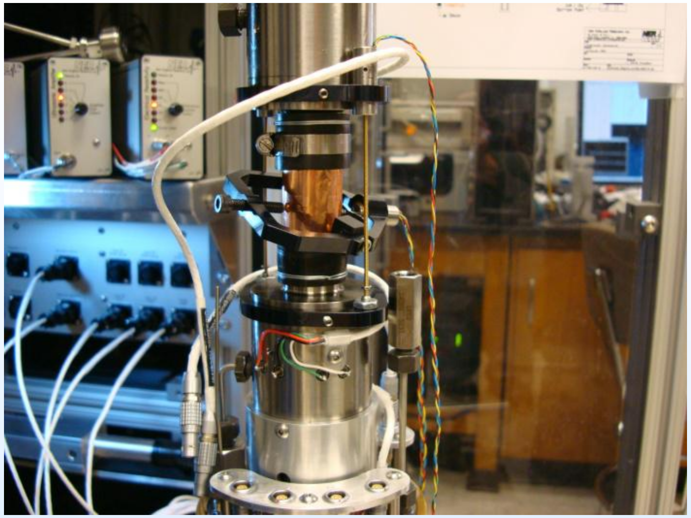




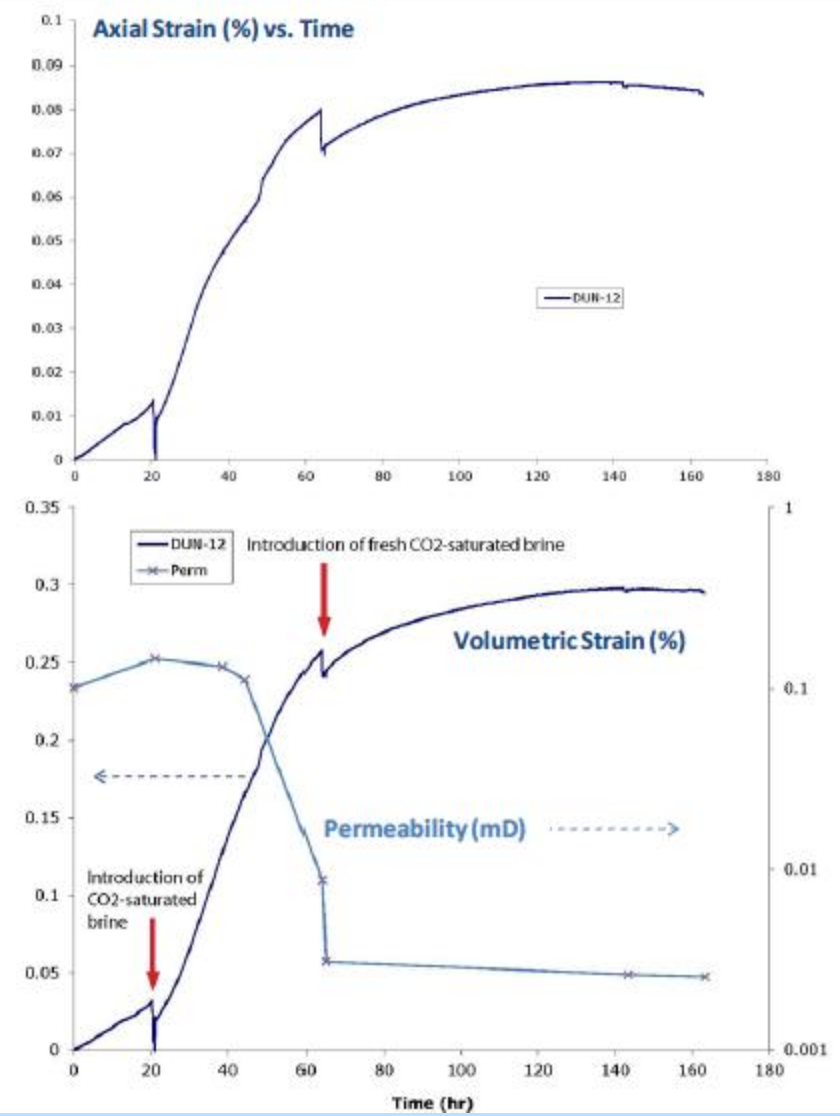




Geo-mechanical experiment and modeling



University of Maryland



Accomplishments to Date

- Completion of a large series of batch runs of geochemical experiments on mineral and rock powders—with different P/T conditions, pH ranges, and grain sizes—to provide data for the thermodynamic database on mineral carbonation reactions, the project's main deliverable.
- Completion of the first geomechanical experiments involving deformation and reactive flow through natural olivine samples.
- Development of a geochemical reaction-rate simulation code and calibration of the code with experimental results using an inverse model.
- Collection and compositional analysis of 9 new natural rock samples from different volcanoes on the Big Island in Hawai'i. These new samples will be used for carbonation experiments on pyroxene and plagioclase, in addition to the extensive experiments already carried out on olivine. Experiments on the new samples will be done in parallel at Yale and at Pacific Northwest National Laboratory (PNNL), in a collaboration started during year 2.

Future directions

- More experiments will be conducted to understand the carbonation rate of plagioclase, clinopyroxene (main constituents of basalts), and rock chips.
- More experiments will be done at lower P-T range for longer time.
- More geo-mechanical experiments involving deformation.
- Flow-through experiments to understand porocity and permeabilty evolution with reaction progress.
- Testing of 1-D and 2-D reactive transport codes for CO_2 saturated fluids flowing through natural and synthetic dunites and basalts.
- Extrapolate our modeling result to predict the outcome of injection at a well-characterized site on big-island Hawaii under various conditions.

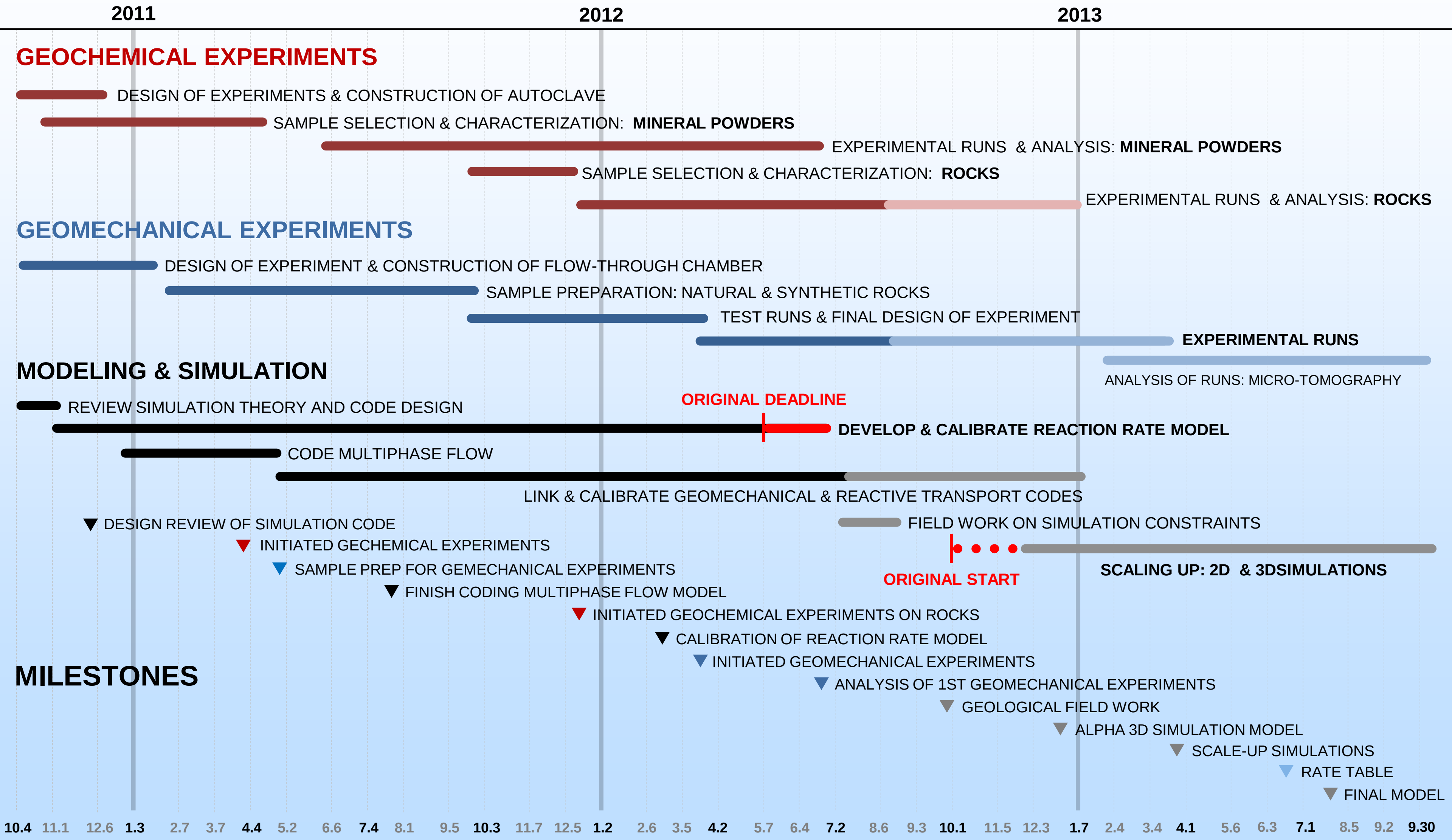
Appendix

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



GEOCHEMICAL EXPERIMENTS

DESIGN OF EXPERIMENTS & CONSTRUCTION OF AUTOCLAVE

SAMPLE SELECTION & CHARACTERIZATION: **MINERAL POWDERS**

EXPERIMENTAL RUNS & ANALYSIS: **MINERAL POWDERS**

SAMPLE SELECTION & CHARACTERIZATION: **ROCKS**

EXPERIMENTAL RUNS & ANALYSIS: **ROCKS**

GEOMECHANICAL EXPERIMENTS

DESIGN OF EXPERIMENT & CONSTRUCTION OF FLOW-THROUGH CHAMBER

SAMPLE PREPARATION: NATURAL & SYNTHETIC ROCKS

TEST RUNS & FINAL DESIGN OF EXPERIMENT

EXPERIMENTAL RUNS

ANALYSIS OF RUNS: MICRO-TOMOGRAPHY

MODELING & SIMULATION

REVIEW SIMULATION THEORY AND CODE DESIGN

ORIGINAL DEADLINE

DEVELOP & CALIBRATE REACTION RATE MODEL

CODE MULTIPHASE FLOW

LINK & CALIBRATE GEOMECHANICAL & REACTIVE TRANSPORT CODES

FIELD WORK ON SIMULATION CONSTRAINTS

ORIGINAL START

SCALING UP: 2D & 3DSIMULATIONS

MILESTONES

- DESIGN REVIEW OF SIMULATION CODE
- INITIATED GECHEMICAL EXPERIMENTS
- SAMPLE PREP FOR GEMECHANICAL EXPERIMENTS
- FINISH CODING MULTIPHASE FLOW MODEL
- INITIATED GEOCHEMICAL EXPERIMENTS ON ROCKS
- CALIBRATION OF REACTION RATE MODEL
- INITIATED GEOMECHANICAL EXPERIMENTS
- ANALYSIS OF 1ST GEOMECHANICAL EXPERIMENTS
- GEOLOGICAL FIELD WORK
- ALPHA 3D SIMULATION MODEL
- SCALE-UP SIMULATIONS
- RATE TABLE
- FINAL MODEL

Bibliography

- No peer-reviewed publications at this time.
- Two submitted manuscripts in review:
  - Cai, Z., and Bercovici, D., 2012, Two-phase damage models of magma- and hydro-fracturing: Earth Planet. Sci. Lett., under revision.
  - Yarushina, V., Bercovici, D., and Oristaglio, M., 2012, Rock deformation models and fluid-leak off in hydraulic fracturing: Geophysical J. Int., under review.
- Three 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 CO_2 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 CO_2-sequestration by olivines and Hawaiian picrites, 22nd V.M. Goldschmidt Conference, June 24–29, Montréal, Canada