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Experiment-Based Model for the Chemical Interactions between Geothermal Rocks, Supercritical Carbon Dioxide and Water

Project Officer: Ava M. Coy
Total Project Funding: $3,000,000
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Track 1 – CO_2

Project objectives

1) Determine **what** chemical interactions occur between relevant minerals and water-CO_2 fluids

2) Understand **how** the chemical interactions affect transition to and performance of a CO_2-EGS

Purpose of the project

- Better assessment of risks associated with an EGS reservoir development using CO_2 as a working fluid;
  - Magnitude of the rock-fluid interactions
  - Location of the geochemical changes
  - Breadth of the interface zone
  - Characterize zone permeability & contact area
- More accurate quantification of the power generation capacity, and prediction of the geothermal production lifetime

Relevance/Impact of Research

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Technical challenges

- Starting materials composition different than expected
- Highly accurate experimental data required for a geochemical model
- Parallel experimentation complicated by diverse dissolution kinetics
- Reactive surface area is changing during the rock-fluid interaction
- Re-mineralization that may occur during an experiment would affect subsequent mineral behavior
- Difficulty in parameterizing complex interactions in the modeling software

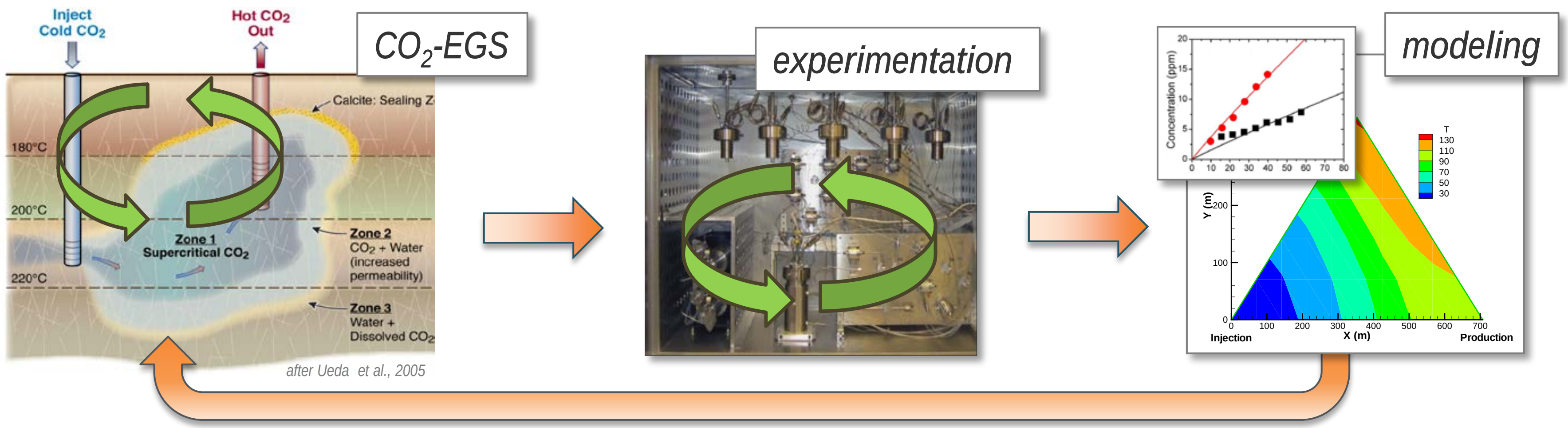
Issues being addressed

- Improve data accuracy and build experimental complexity into the models
- Understand the surface area effect and adopt it into rock-fluid interaction model
- Specific issues related to behavior of rocks from the Cranfield CO_2 injection site

Scientific/Technical Approach

Technical approach

1) Build a multi-channel batch system and generate mineral solubility data (2011/12)
2) Upgrade the system by adding a circulation flow-through channel (mid 2012)
3) Simulate the injection-production cycle to advance the CO_2-EGS model (finishing)
4) Conduct SEM analysis on pre- and after-reaction mineral samples and compare the changes in textures and mineralogy (ongoing)
5) Experiment using rocks from actual CO_2 injection site at Cranfield, MS (ongoing)
6) Create the experiment-based model (ongoing)



Accomplishments, Results and Progress

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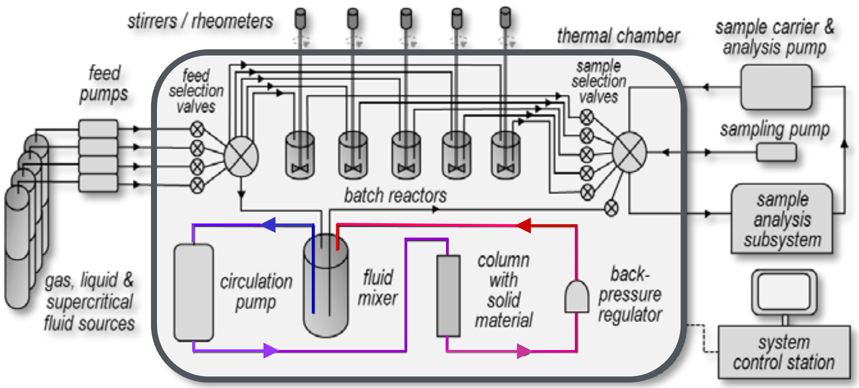
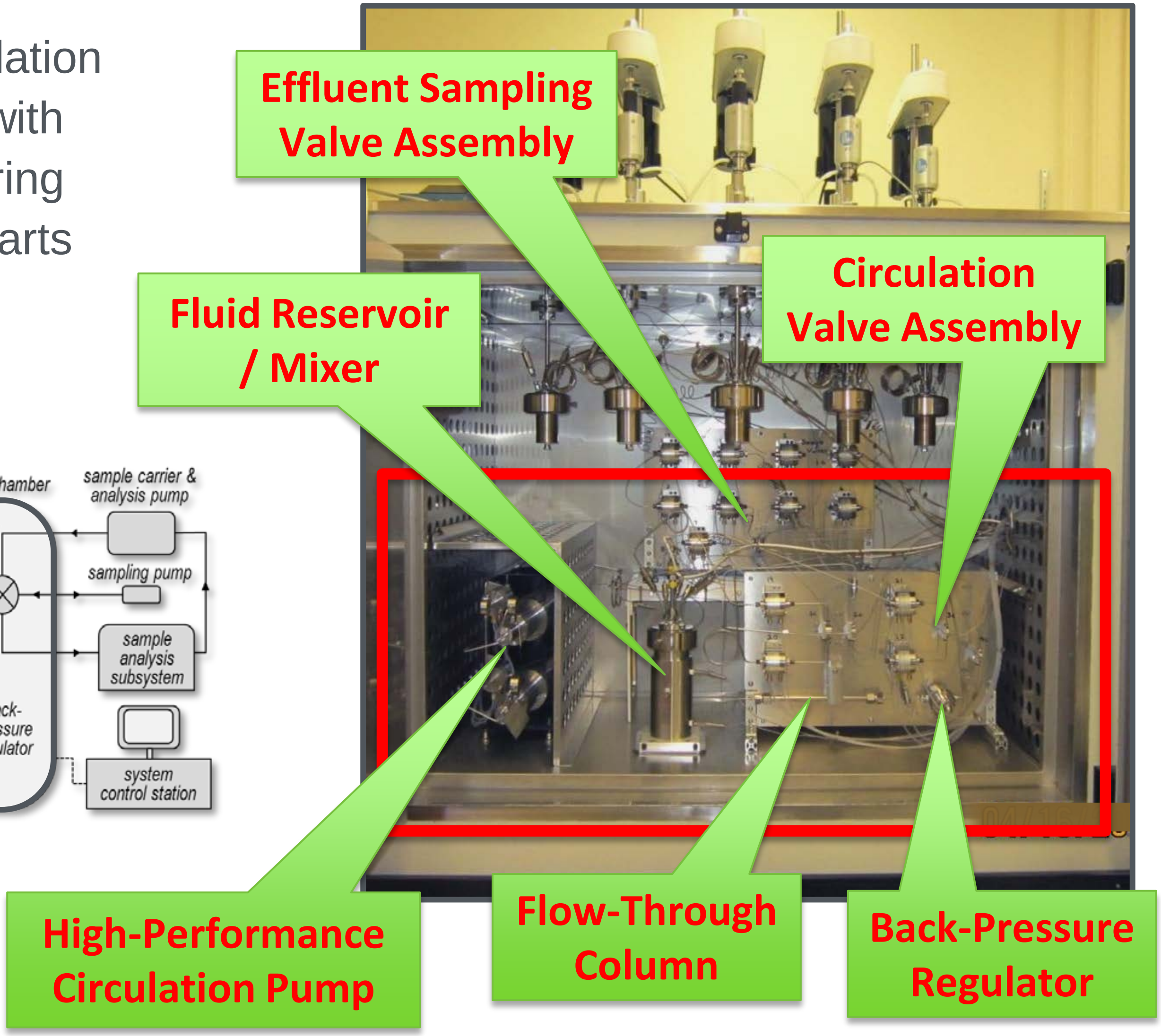
1) Generated a solubility map for relevant minerals under various CO_2-water & PT conditions
2) Added a flow-through channel and synchronized it with all five batch reactors built earlier
3) Determined effects of the particle size and surface area of minerals on dissolution kinetics
4) Improved ion detection sensitivity to identify conditions for dissolution of low-solubility minerals
5) Evaluated changes in mineral textures due to mineral dissolution / precipitation by SEM
6) Obtained kinetic parameters from the batch experiment data for key geothermal minerals
7) Discovered unexpected behavior of some minerals in CO_2-water at high temperature
8) Assessed complexity of a real rock sample through behavior of its individual components
9) Performed reactive transport modeling of changes in geological conditions of an EGS
10) Turned experimental findings on rock-fluid interactions into a model of real CO_2 injection site

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Add and validate flow-through channel	Works in-sync with five other reactors	6/30/2012
Develop rock characterization workflow	Included new particle sizing methodology	7/31/2012
Perform experiments with water-CO_2 fluids circulation through a rock bed	Included a real rock sample from the existing CO_2 sequestration site (Cranfield)	to be completed 4/31/2013
Develop an experiment-based model of an EGS transition from water to CO_2	Initial reactive transport modeling already performed and adopted to a real setting	to be completed 7/31/2013

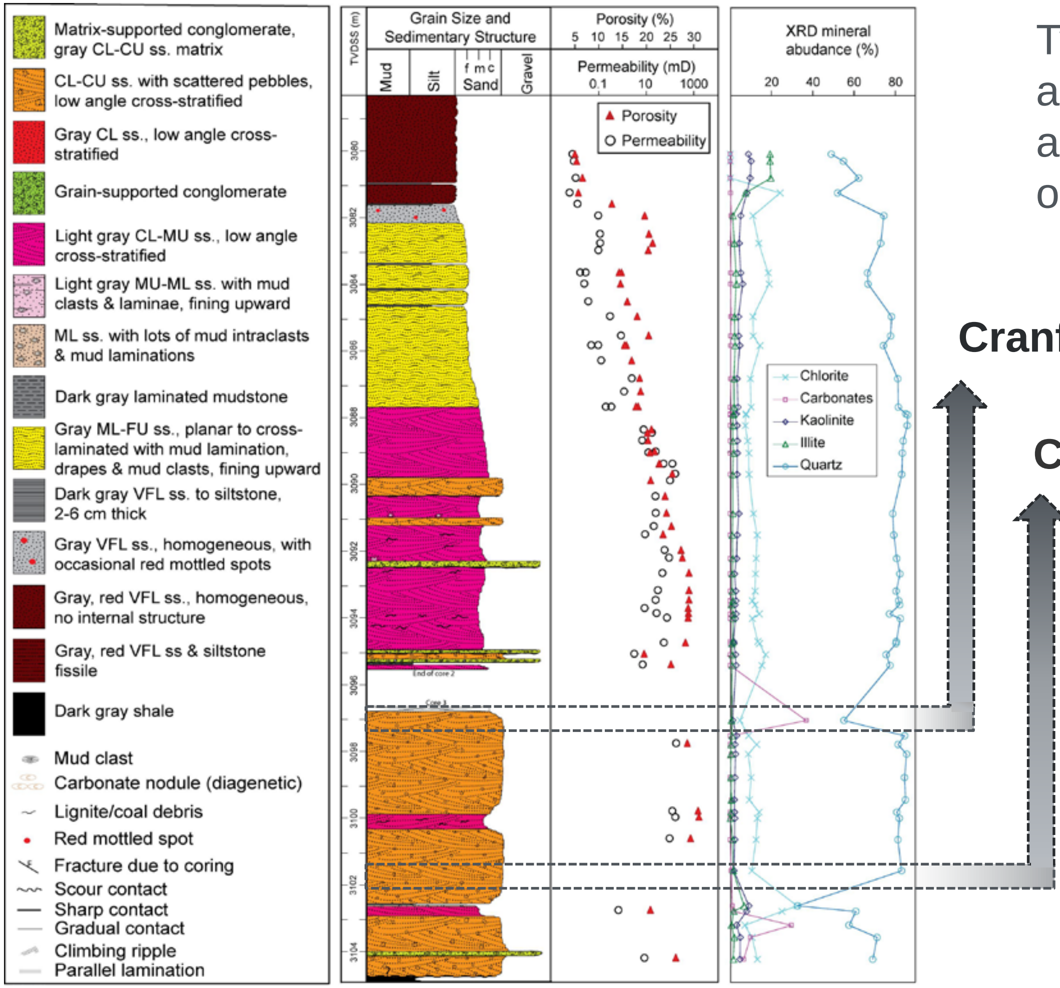
Experimental system upgrade

New continuous flow / circulation channel operates together with the five batch reactors, sharing the feeding and analytical parts of the complete system.





Cranfield rock samples composition



Picture from: J. Lu, M. Kordi, S.D. Hovorka, T.A. Meckel, C. A. Christopher "Reservoir characterization and complications for trapping mechanisms at Cranfield CO2 injection site" by, currently in press for the Special issue on Cranfield in International Journal of Greenhouse Control.

Two Cranfield rock samples obtained as a courtesy of Prof. Susan Hovorka and Dr. Jiemin Lu from the University of Texas at Austin

Cranfield Sample #1 - more carbonates

Cranfield Sample #2 - more chlorite

! **Chlorite & Illite**: very little known, presumably of very low solubility !

Calcite & Dolomite: well known as highly soluble in water-CO_2

Kaolinite: quickly disintegrates into 100 nm nanoparticles

Quartz: practically insoluble

Effect of mineral granularity on dissolution

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Particle size bins

▲ 25-63 µm
■ 63-150 µm

Surface area measurement

BET method
(argon absorption)

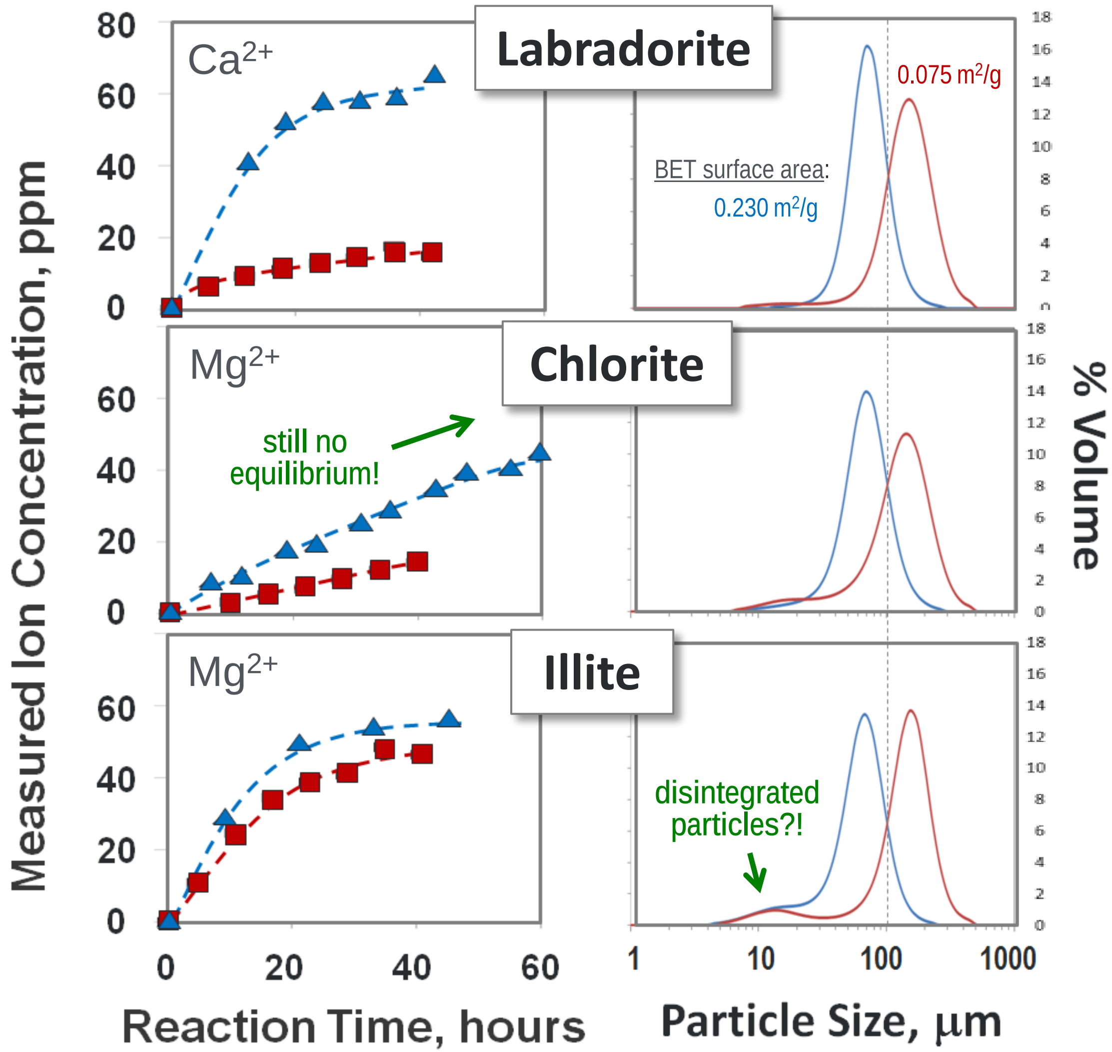
Particle size distribution

Multi-angle light scattering

Dissolution Conditions

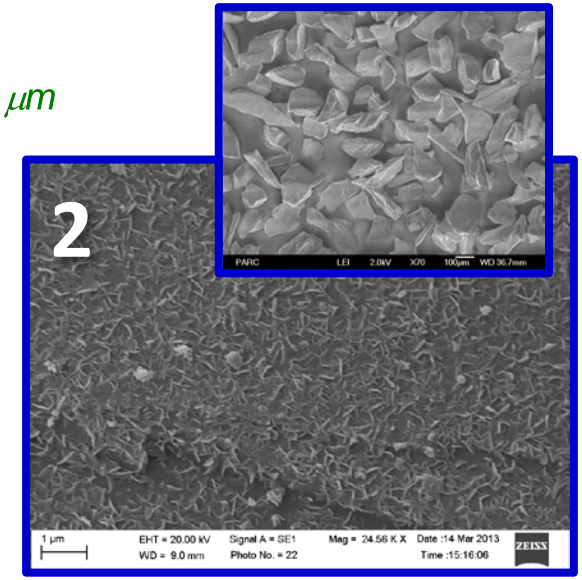
PARC rock-fluid system
Fluid: CO_2-saturated water
Temperature: 150 °C
Pressure: 1,200 psi

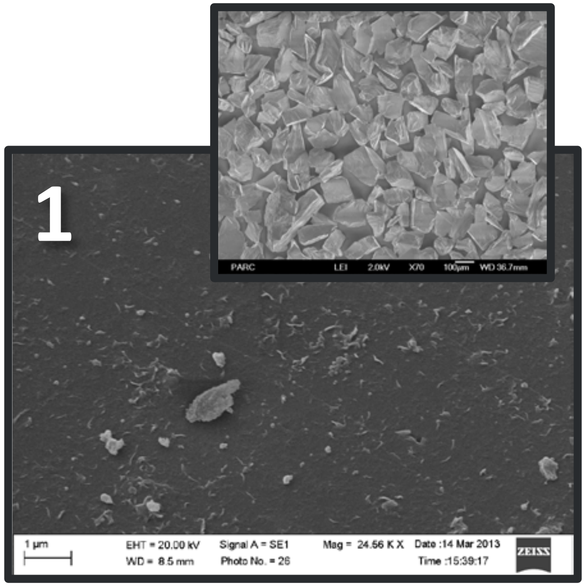
Mineral Dissolution Profiles ***Particle Size Distributions***

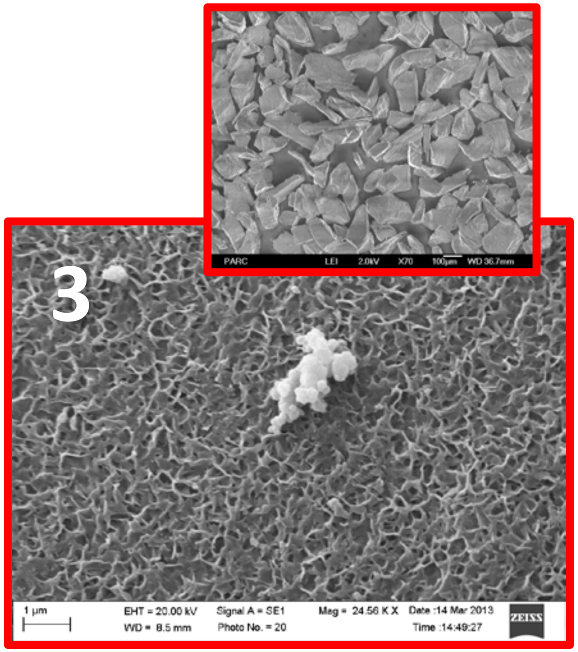


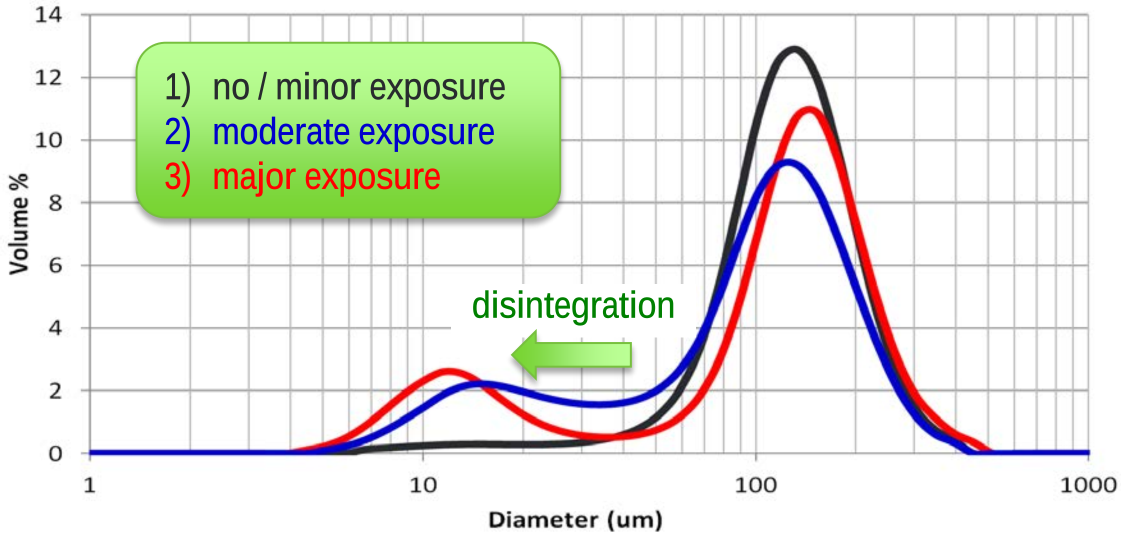
Labradorite

- *Sieved into particle size range 63-150 μm*
- *Exposure to 120/150 ^oC water-CO_2 for up to 240 hours*
- *Particle size distribution by MALS*
- *Particle imaging by SEM*







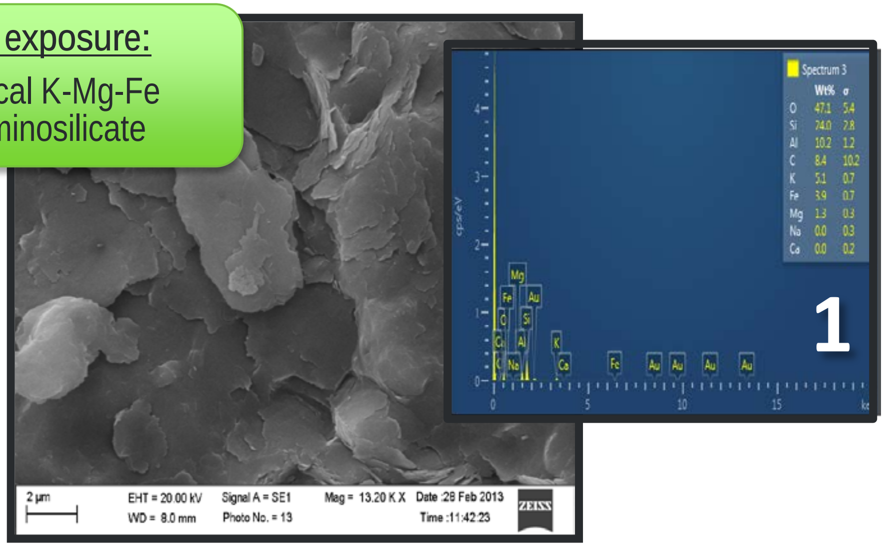


Compositional changes during dissolution

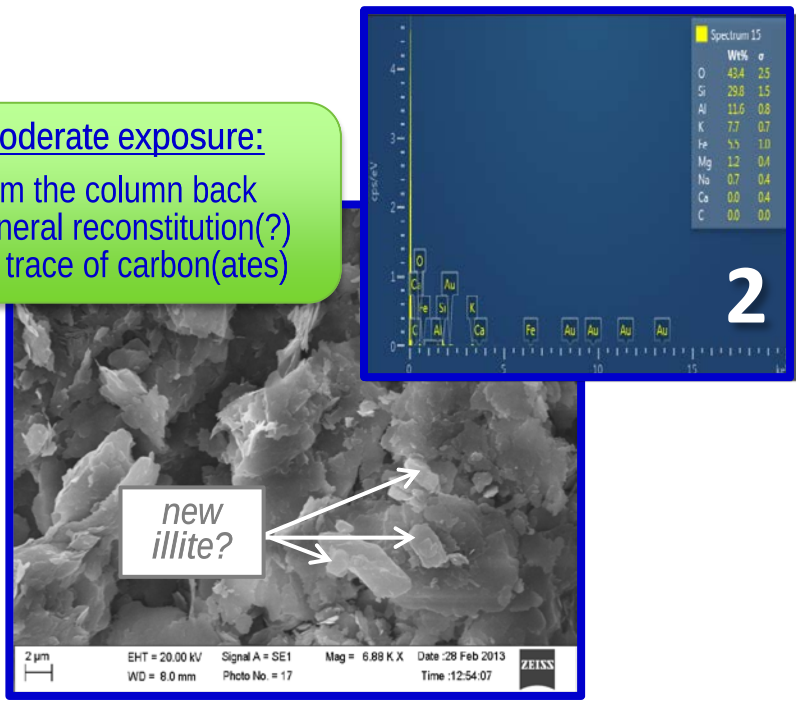
Illite

- *Sieved into particle size range 63-150 μm*
- *Complex chemical composition expected* $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
- *240 hr exposure to 120/150 ºC water-CO_2*
- *Spot elemental analysis by EDS*
- *Particle imaging by SEM*

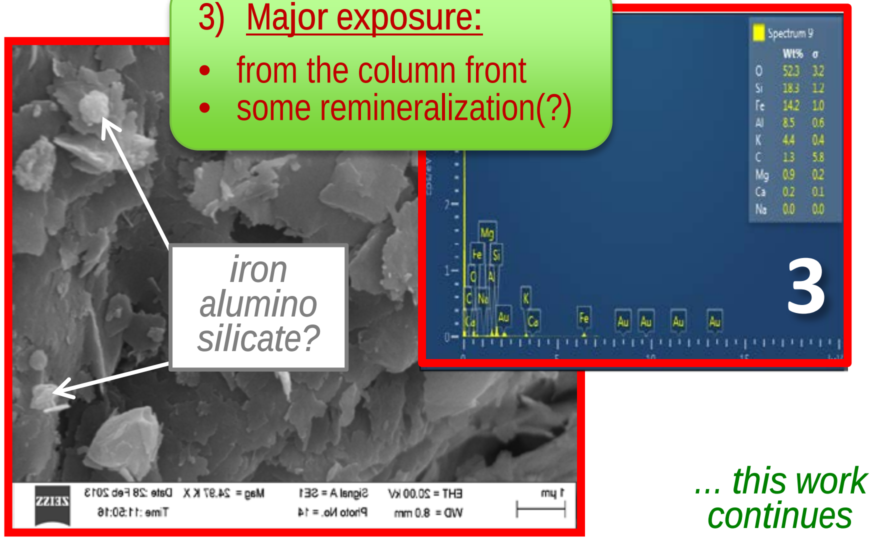
1) No exposure:
- typical K-Mg-Fe aluminosilicate



2) Moderate exposure:
- from the column back
- mineral reconstitution(?)
- no trace of carbon(ates)



3) Major exposure:
- from the column front
- some remineralization(?)



... this work continues

Mineral solubility response to temperature

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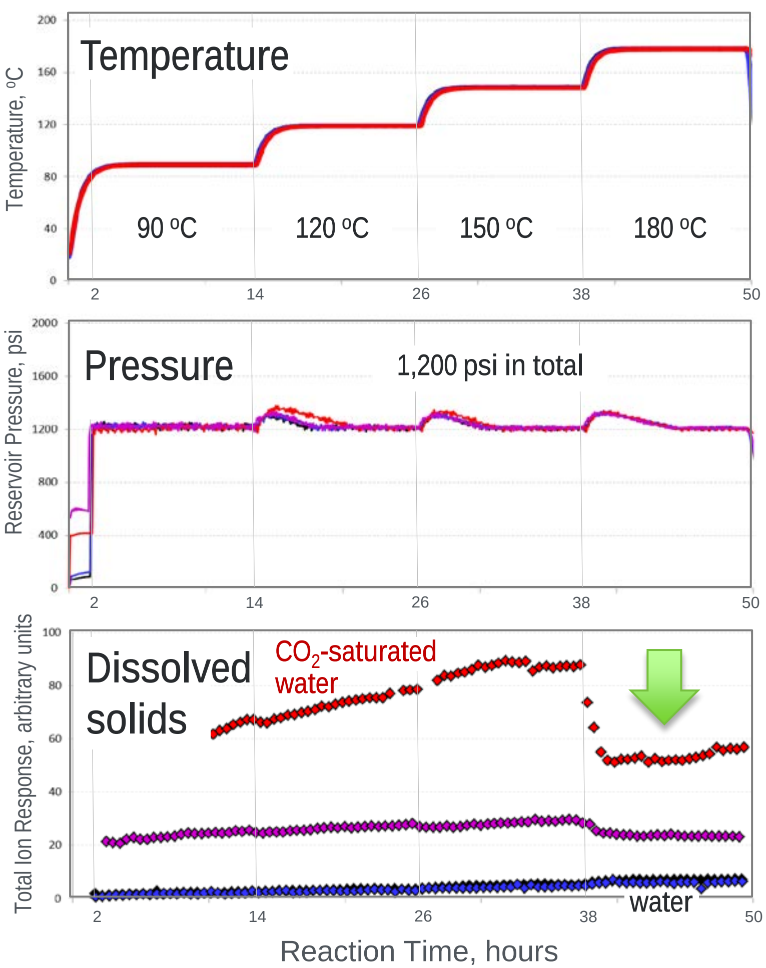
Illite

$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}$ $[(OH)_2,(H_2O)]$, 63-150 µm



<u>Reactor system setting</u>: Continuous flow channel in circulation mode at 3 mL/min, with 600 mL fluid reservoir and 20 mL mineral column

<u>Set temperature</u>: 90, 120, 150 up to 180 °C in 12 hr steps

<u>Set total reservoir pressure</u>: 1,200 psi maintained by helium

<u>Dissolved mineral response</u>: Total ion peak are as detected by on-line ion chromatography

<u>Fluids and Pressures</u>: **500mL water** pressurized up to **1,200 psi helium** with various partial pressures of CO_2 for

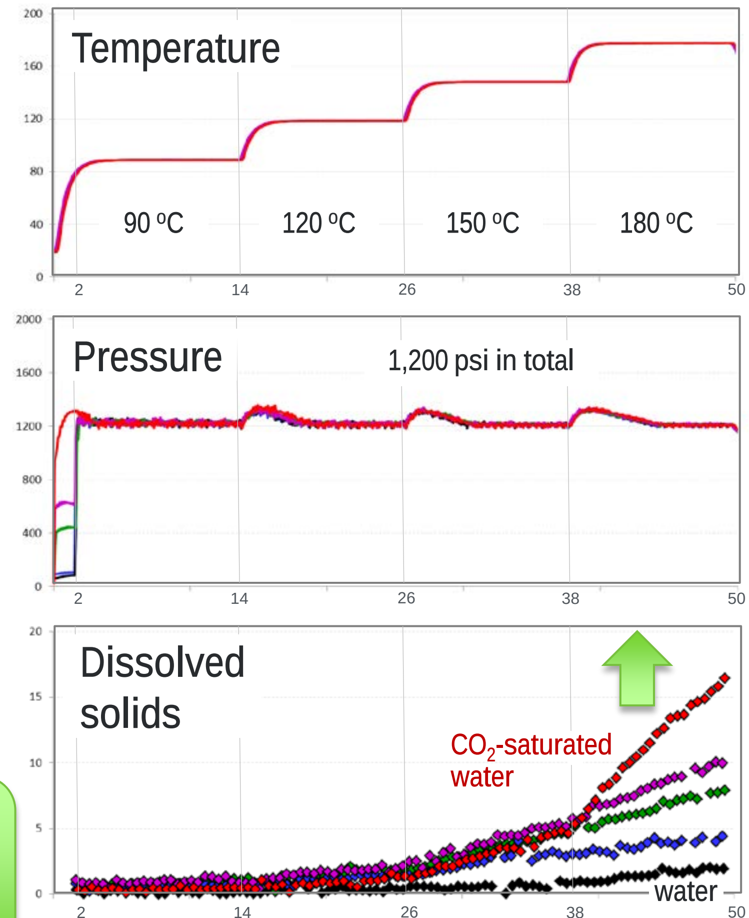
illite: and	*chlorite*:
0 psi CO_2	0 psi CO_2
62 psi CO_2	90 psi CO_2
88 psi CO_2	400 psi CO_2
600 psi CO_2	600 psi CO_2
1200 psi CO_2	1200 psi CO_2

Surprises at 150→180 °C

1. drop in illite solubility
2. accelerated dissolution of chlorite, no equilibrium

Chlorite

$Mg,Fe,Ni,Mn,Al/(AlSi_3)$ $O_{10}(OH)_8$, 63-150 µm



… Cranfield sample evaluation still ongoing

Initial model of 20-yr transition to CO_2-EGS

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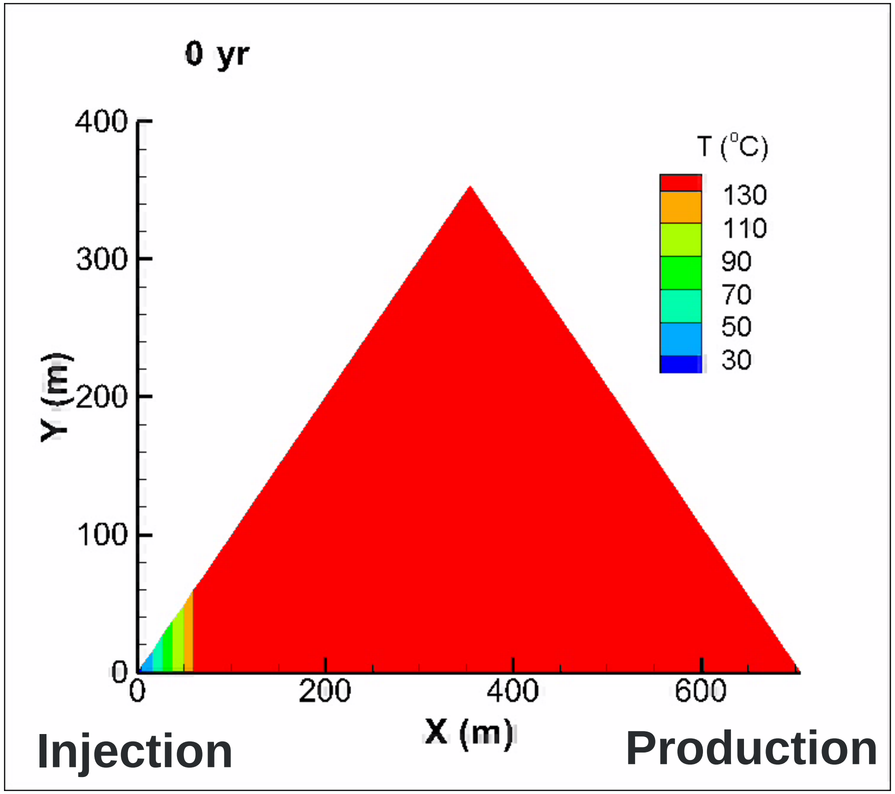
Simulation of temperature changes over 20 years of recycled CO_2 injection in a Cranfield-like reservoir



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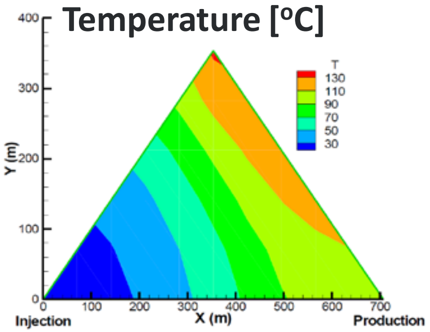
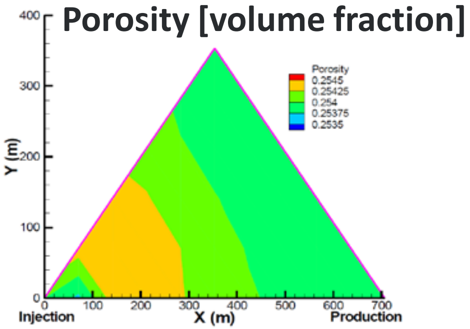
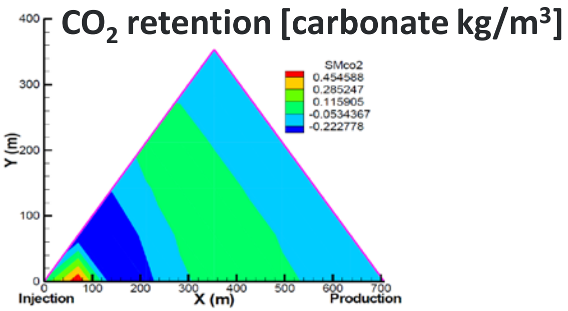
20-year status of changes in the Cranfield-like CO2-EGS reservoir





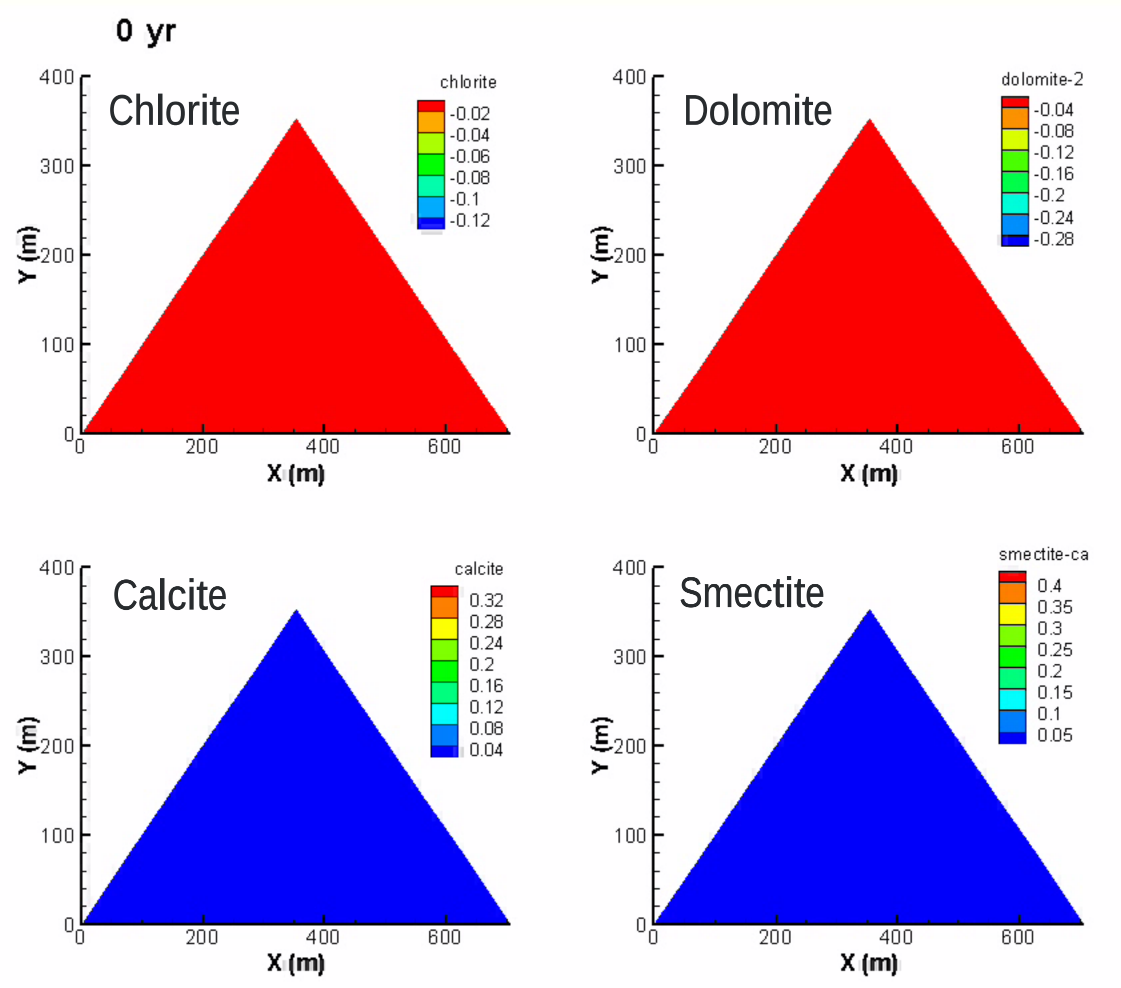


20-yr change in mineral composition

Simulation of mineral composition changes in a Cranfield-like reservoir over 20 years of recycled CO_2 injection

The starting mineralogical composition in volume fraction is based on literature data *(Lu et al, J. Greenhouse Ctrl., in press):*

Mineral	Volume Fraction
Quartz	0.794
Chlorite	0.118
Kaolinite	0.031
Illite	0.013
Calcite	0.011
Dolomite	0.004
Albite	0.002
Non-reactive	0.027



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Future Directions

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- Key activities to project completion in July 2013:
  - Finish the ongoing experiments (chlorite equilibrium and Cranfield sample)
  - Hand over the experimental data to LBNL (raw and reduced up to date)
  - Further characterize pre-/post-experiment samples (Cranfield, chlorite, illite)
  - Adopt the experimental findings into the reactive transport modeling effort
  - Refine existing geochemical models further (reactive surface area evolution)
  - Create a new CO_2-EGS model around the Cranfield reservoir setting

Milestone or Go/No-Go	Status & Expected Completion Date
Perform experiments with water-CO_2 fluids circulation through a rock bed	Included a real rock sample from the existing CO_2 sequestration site at Cranfield, MS (to be completed by 4/31/2013)
Develop an experiment-based model of an EGS transition from water to CO_2	Initial reactive transport modeling already performed and adopted to a real setting (to be completed by 7/31/2013)
Complete the project	7/31/2013

Mandatory Summary Slide

- The kinetics can mislead the thermodynamic measurements as slowing down may often look like reaching an equilibrium
- Trace level components may easily overshadow the effect of major ones, requiring separation-based detection to deconvolve
- Even the simplest physical / chemical interactions can become overwhelmingly complex if changes affect the process itself
- Accuracy of rock-fluid interaction data is the critical factor for realistic modeling of a geothermal reservoir in transition
- Modeling can hardly capture complexity of multicomponent dynamic rock-fluid interactions without an experimental input

Project Management

- The initial delay due to program Novation from original awardee to PARC
- The financial information corresponds to the 2/28/2013 status:

Timeline:

Planned Start Date	Planned End Date	Actual Start Date	Current End Date
December 29, 2009	December 31, 2012	August 9, 2010	July 31, 2013

Budget:

Federal Share	Cost Share	Planned Expenses to Date	Actual Expenses to Date	Value of Work Completed to Date	Funding needed to Complete Work
$3,000,000	$1,004,705	$3,000,000	$2,704,782	$3,433,390	$295,218

- Everything proceeds according to the plan updated at Novation:
  - PARC prepares for completing the experimental work
  - Modeling activities at PARC accelerate
  - The workload and corresponding funding is to shift towards LBNL
  - Interacting with industry leaders and still looking for opportunities
- We expect to complete the whole project in time and within the budget