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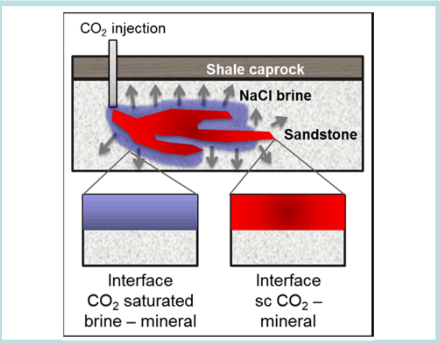

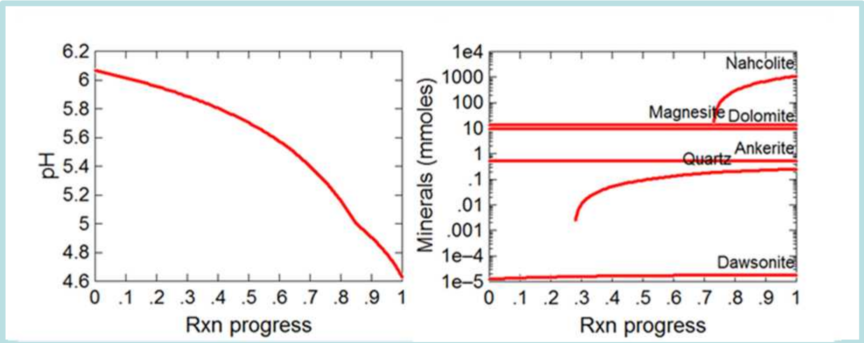

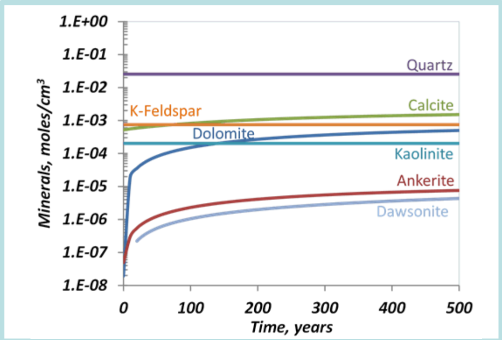

Geologic sequestration of CO_2: mineral dissolution and precipitation during CO_2 injection at the Frio-I brine pilot

Anastasia G. Ilgen

November 12, 2014

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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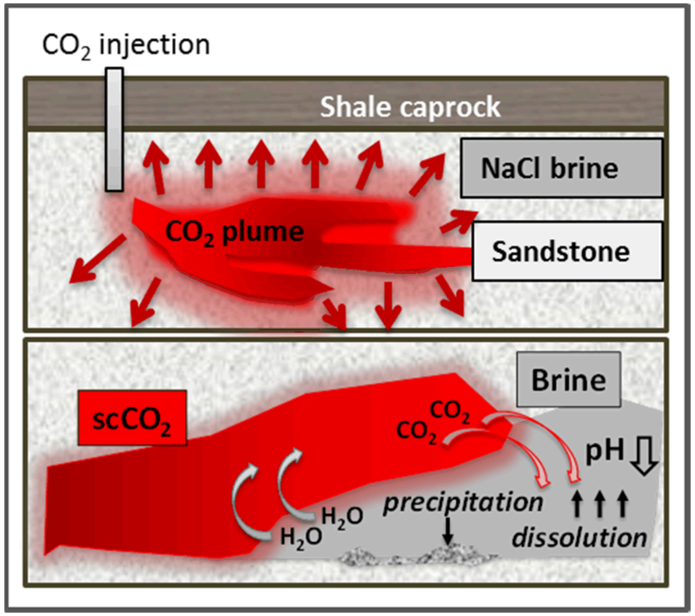
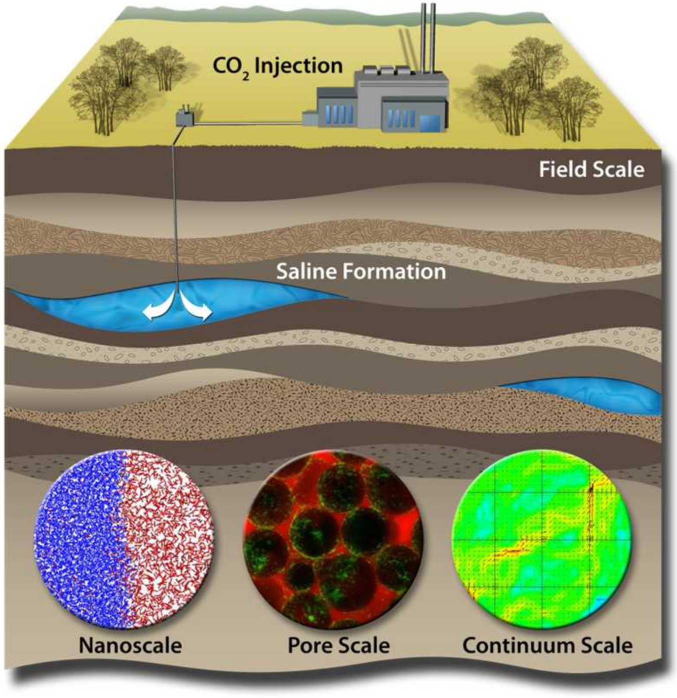
Outline

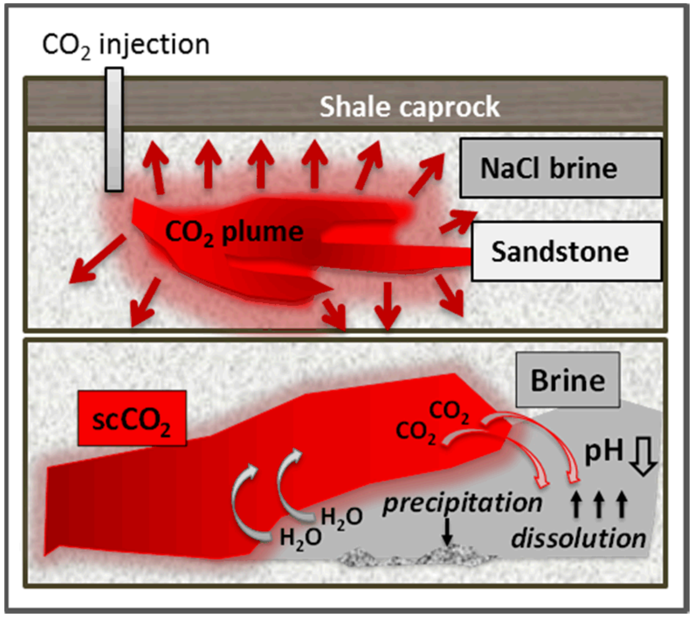
Mineral Dissolution and Precipitation during CO_2 Injection at the Frio-I Brine Pilot



Overview Center for Frontiers of Subsurface Energy Security (CFSES)

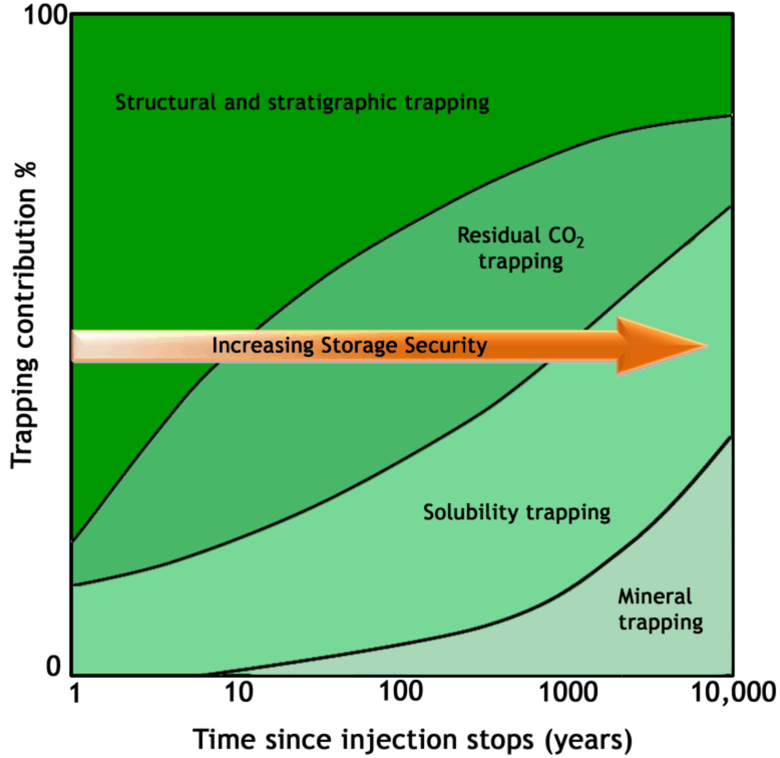


Mineral Dissolution and Precipitation during CO_2 Injection at the Frio-I Brine Pilot: Geochemical Modeling and Uncertainty Analysis



Geologic sequestration of CO_2

- Feasible methods for decreasing atmospheric carbon dioxide (CO_2). [1-5]
- Natural analogs for CO_2 storage are stable and retain CO_2 on geologic time scales. [2]
- Solubility trapping is the predominant CO_2 sink. [6]
- Crucial features: sufficient porosity, and continuous and fracture-free cap rock.
- Deep saline reservoirs - one of the top candidate formations for geologic storage of CO_2. [1, 2]



[1] DePaolo et al., 2013
[2] Marini, 2006
[3] Kharaka and Cole, 2011
[4] Kobos et al., 2011
[5] Steele-MacInnis et al., 2012
[6] Gilfillan et al., 2009

Geochemical response triggered by the injection of CO_2

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- At the deep geologic storage PT: CO_2 is stable in its supercritical (sc) state.
- $scCO_2$ stimulates **geochemical responses**: acidification of parent brine, and dehydration of mineral surfaces by the dispersing $scCO_2$ phase.[1-3, 8]
- Experimental and field studies: geochemical reactions differ significantly for different rock assemblages and brine compositions.[7-9]
- Typical low-permeability cap rocks (e.g. shale) are reactive at the higher end of the geologic carbon storage temperature range.[10, 11]
  - Dissolution and re-precipitation of **carbonate minerals**, dissolution of **feldspars**, and precipitation of **clay minerals**.[10]
- Dissolution and secondary mineral precipitation control the evolution of **porosity** and **permeability** [8], with potential impact on the cap rock integrity, and CO_2 leakage.[10, 12]

[1] DePaolo et al., 2013
[2] Marini, 2006
[3] Kharaka and Cole, 2011
[4] Kobos et al., 2011
[5] Steele-MacInnis et al., 2012
[6] Gilfillan et al., 2009
[7] Bickle et al., 2013
[8] Jun et al., 2012
[9] Lu et al., 2012
[10] Liu et al., 2012
[11] Kaszuba et al., 2003
[12] Harvey et al., 2012

Frio-I Pilot in 2004

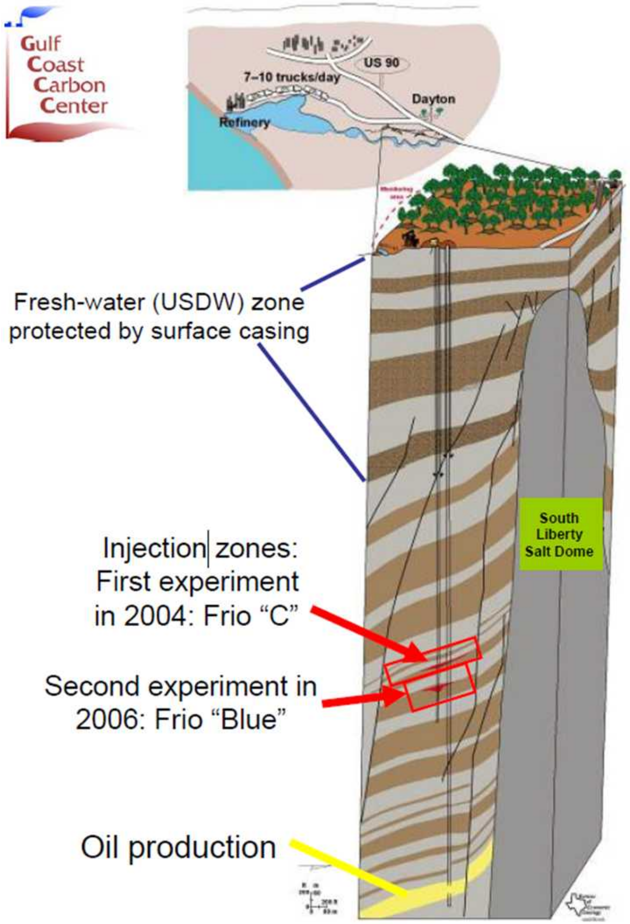

Figure from presentation by T. Meckel (2008)

- Setting: salt dome flank, Frio sandstone;
- 1600 tons at 3 kg/s, 10 day injection in 1545 m deep well;
- ~ 40 water samples collected for 4 days using 1530 m deep monitoring well.

Minerals

Quartz	Oligoclase	Illite
Kaolinite	K-feldspar	Na-smectite
Calcite	Chlorite	Hematite

Water chemistry

Component	Concentration (mol/kg H_2O)
Ca^{2+}	6.6×10^{-2}
Mg^{2+}	2.2×10^{-2}
Na^{+}	1.35
K^{+}	4.53×10^{-3}
Iron	4.63×10^{-4}
$SiO_2(aq)$	2.50×10^{-4}
Carbon	5.04×10^{-2}
Sulfur	4.20×10^{-5}
Al^{3+}	1.56×10^{-8}
Cl^{-}	1.49
$O_2(aq)$	4.88×10^{-68}
pH	6.7
Temperature	59 °C

Water chemistry observations and modeling

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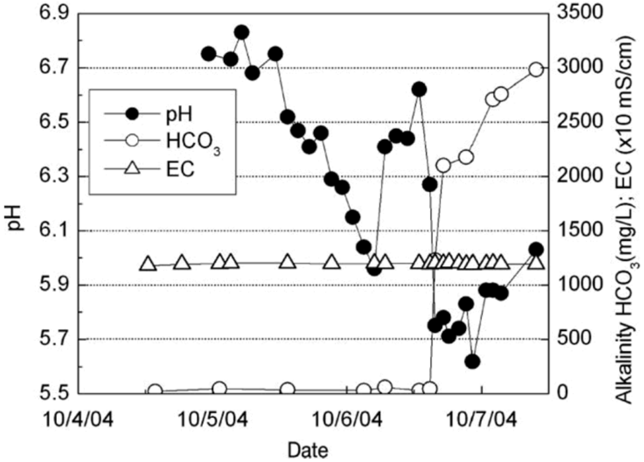
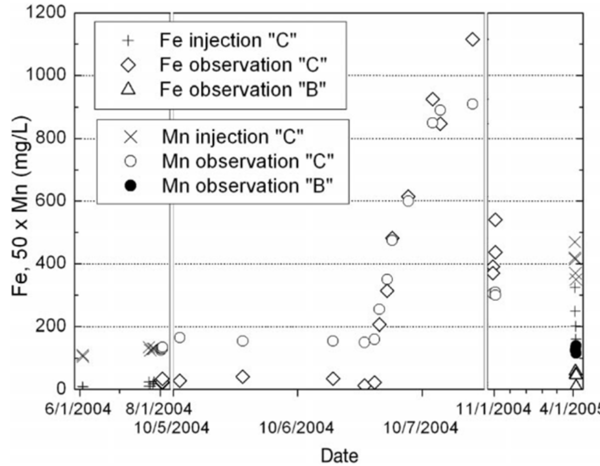
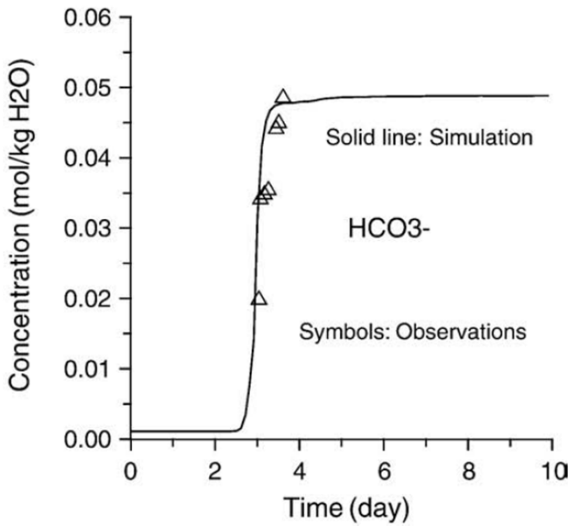
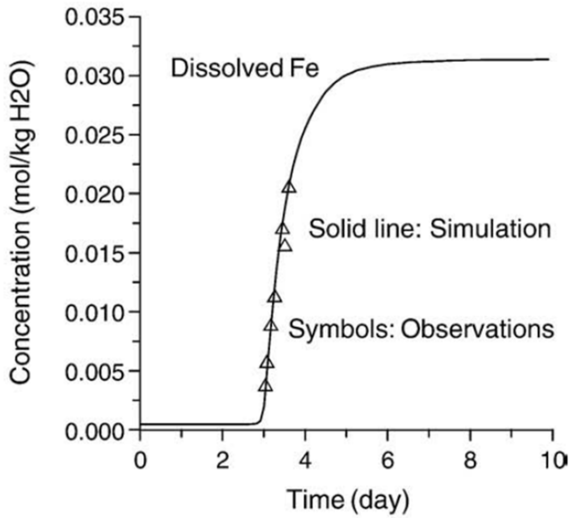




- pH drop ↓ 6.5 to 5.7;
- Alkalinity ↑ 100 to 1100 mg/L;
- Fe ↑ 30 to 1100 mg/L;
- Mn and Ca ↑

Figures from Kharaka et al. (2006) Geology, 34, 577



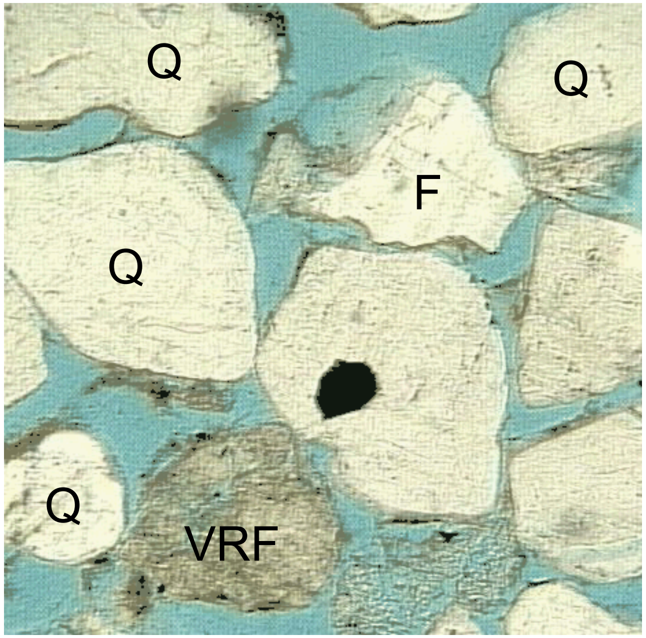


- Existing models capture changes in inorganic chemistry, Fe in particular, in the observation well over time.
- Conclude: fast dissolution of calcite and Fe oxide.

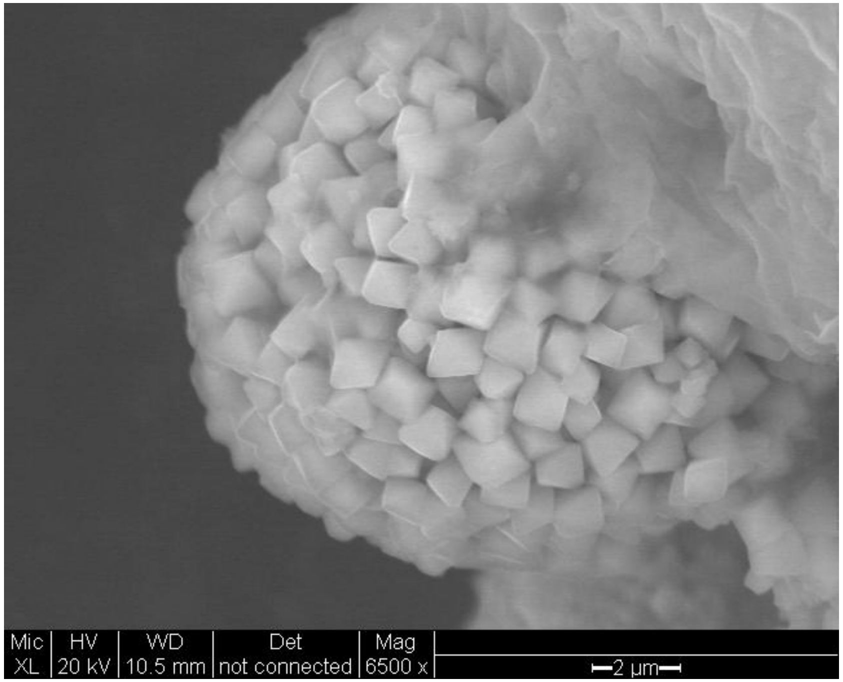
Figures from Xu et al. (2010) Chem. Geol., 271, 153

Petrographic observations

- Calcite cement in Frio Formation varies and can be absent.
- Petrographic study of the Upper Frio Formation "C" found no calcite cement.
- Frio Formation "C" sandstone contains 24 wt. % of feldspar, mostly **anorthite** $CaAl_2Si_2O_8$.



Quartz (Q), feldspar (F), and volcanic rock fragments (VRF)



Framboidal pyrite

- No crystalline iron oxyhydroxides.[23]
- Abundant fine-crystalline **pyrite** FeS_2.[23]

Images from McGuire (2009) MS thesis: "CO_2 Injection and Reservoir Characterization: an Integrated Petrographic and Geochemical Study of the Frio Formation, Texas.

Objectives:

- To test the hypothesis that increase in **iron** could be due to the **dissolution of pyrite**; and increase in **calcium** - to the **dissolution of anorthite**.

- If dissolution of pyrite and anorthite were likely, incorporate these reactions into the **long-term (1000 years) reactive transport model** to account for precipitation of carbonates (specifically, calcite and siderite).

- Explore the range of **uncertainty** due to indeterminate rate constants for the pyrite, calcite, and anorthite dissolution, and compare the range of predicted values to the actual observations recorded during the Frio-I Brine Pilot.

Method:

- Path of reaction and reactive transport modeling using Geochemists Work Bench (Bethke, 1998).

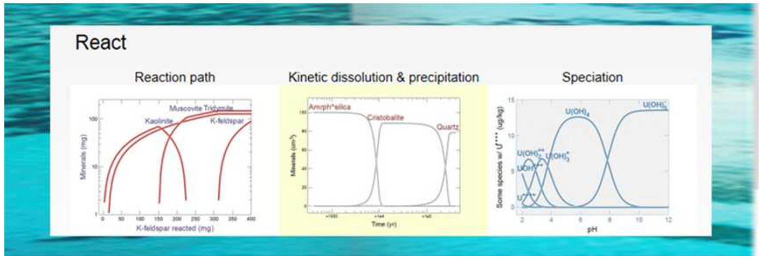


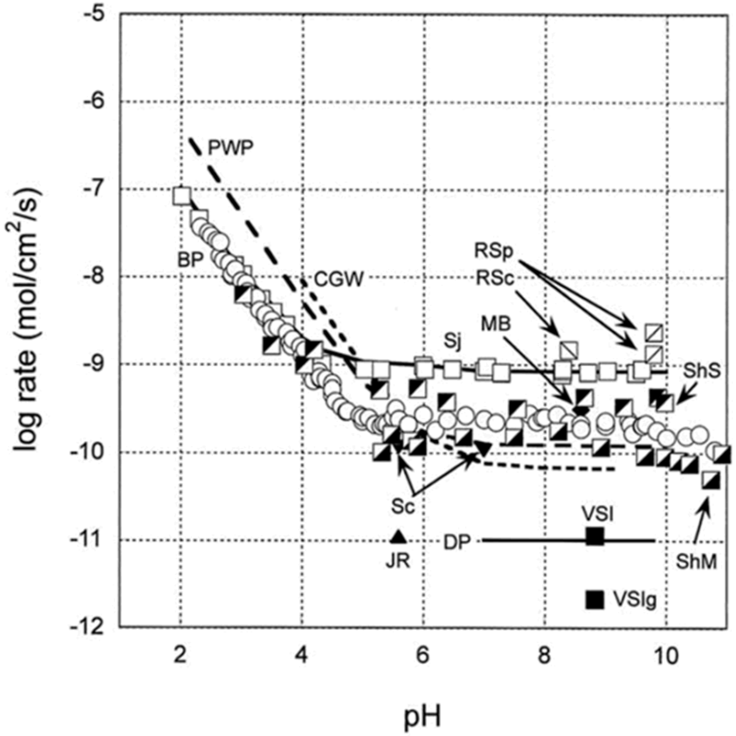
Image source: http://www.gwb.com/

Challenges in geochemical modeling of geologic CO_2 sequestration

Marini L. (2007) Geological Sequestration of Carbon Dioxide: Thermodynamics, Kinetics, and Reaction Path Modeling.

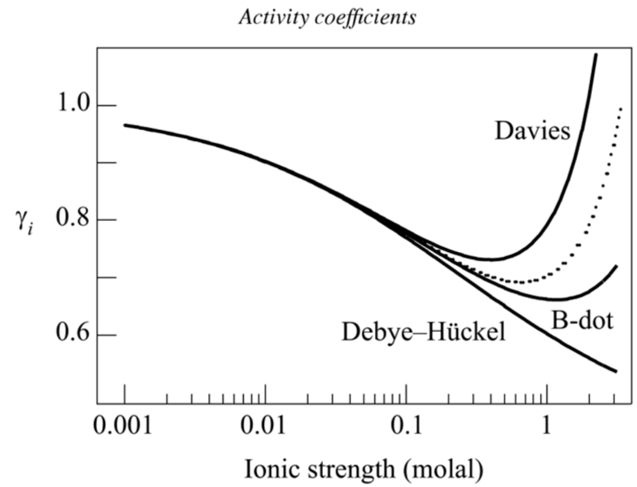
- Inadequate **activity** correction;
- Unknown **thermodynamic properties** of relevant mineral phases;
- Uncertain reaction **kinetics**;
- Deficiencies in knowledge of **nucleation** and crystal growth;
- Uncertain reactive **surface areas**.

Calcite dissolution rates



Arvidson et al. (2003) Geochimica et Cosmochimica Acta, 67, 8, 1623

Activity correction



$$\mu_i \equiv \frac{\partial G_i}{\partial n_i} = \mu_i^{\text{o}} + \text{R}T_{\text{K}} \ln \gamma_i m_i$$

Debye-Hückel methods
Works for I < 0.1 m

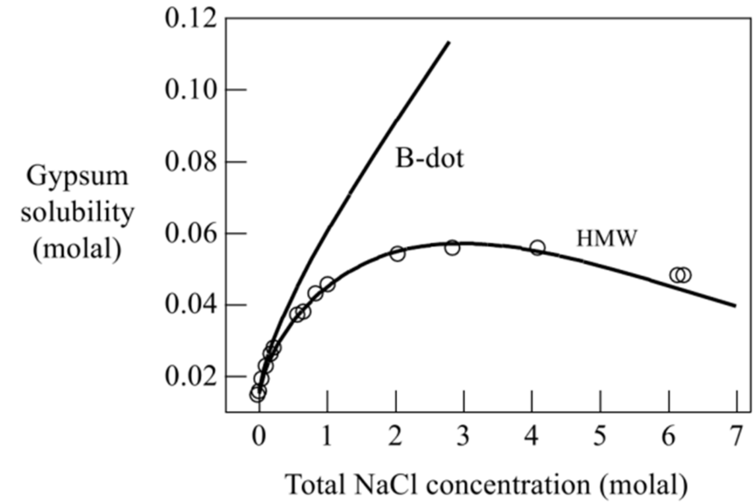
$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + \mathring{a}_i B \sqrt{I}}$$

Davies method
Works for I =0.3-0.5 m

$$\log \gamma_i = -A z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$$

B-dot method
Works for I = 0 - 3 m Na^+ and Cl^-,
0.3 – 1 m other ions

$$\log \gamma i = -\frac{A z i^2 \sqrt{I}}{1 + a i B \sqrt{I}} + \dot{B} I$$



Virial methods

$$\ln \gamma_i = \ln \gamma_i^{\text{dh}} + \sum_j D_{ij}(I) m_j + \sum_j \sum_k E_{ijk} m_j m_k$$

← *e.g. Harvie-Møller-Weare (HMW)*

Figures from Bethke, 2008

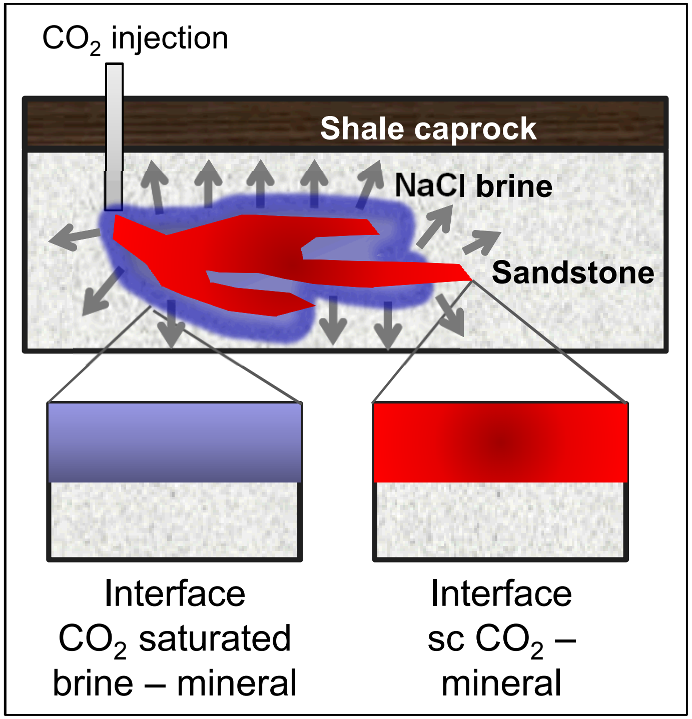
Updated thermodynamic database

- Modified EQ3/6 v. 8.0 (*Wolery, 1992*). Pitzer activity correction method.
- 20 elements: O, **Al**, B, Br, C, Ca, Cd, Cl, F, Fe, H, K, Li, Mg, Mn, **N**, Na, **P**, S, **Si**.
- Updated carbonate solubility:
  - ✓ dolomite (Holland and Powell, 1998);
  - ✓ magnesite (Holland and Powell, 1998);
  - ✓ hydromagnesite (Robie and Hemingway, 1995);
  - ✓ dawsonite (Benezeth et al. 2007);
  - ✓ siderite (Benezeth et al. 2009);
  - ✓ added ankerite (Holland and Powell, 1998);
  - ✓ ΔG and ΔH values for HCO_3^- species from (Robie and Hemingway, 1995).

Pitzer parameters are represented by the four term temperature function given by:

$$x(T) = a1 + a2\times(1/T - 1/298.15) + a3\times\ln(T/298.15) + a4\times(T - 298.15) \quad (1)$$

where T is temperature in Kelvin and a1 through a4 denote the temperature function fitting coefficients for the temperature dependent Pitzer parameters.



CO_2 injection creates

two new distinct **geochemical interfaces**:

1) Supercritical CO_2 – mineral interface:

H_2O activity is decreasing

2) CO_2 saturated brine – mineral:

$CO_2(aq)$ is increasing

Reaction Path Modeling

Goal: Configure models to predict shifts in pH and mineral saturation

- Aqueous + mineral components, sweep along increasing dissolved CO_2
- Aqueous + mineral components, constant aq. CO_2 and sweep along decreasing H_2O.

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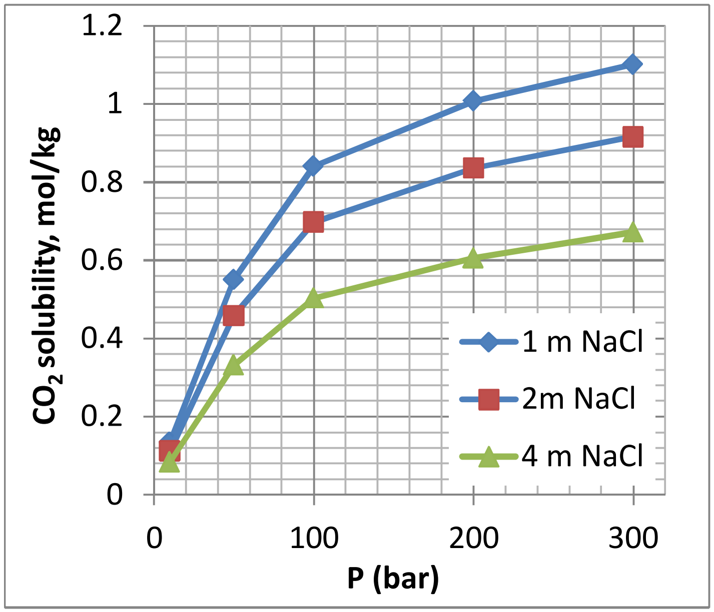
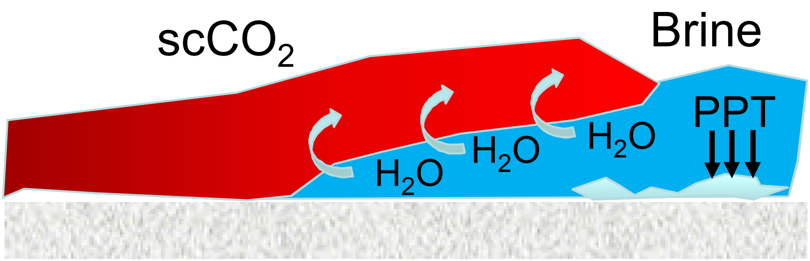
Boundary condition 1: Solubility of CO_2 in brine



Duan and Sun (2003) Chem Geo 193, 257

- Estimated CO_2 solubility at 333.15 K, 150 bar, 1.6 M NaCl **0.82 M**

Boundary condition 2: amount of H_2O available after the system is dehydrated due to CO_2 injection



- Assumed maximum **90 wt. %** of H_2O is removed due to "drying" by CO_2

Reactive Flow Model

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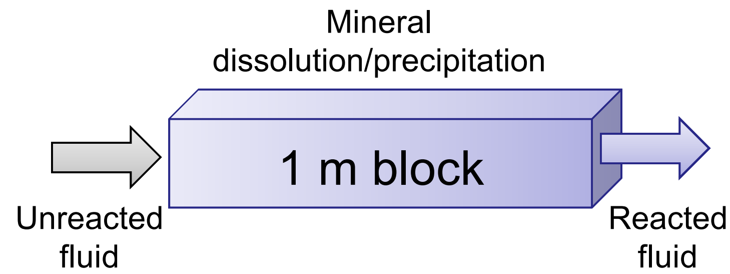
Goal:

To predict long-term mineral dissolution and precipitation after the emplacement of CO_2 in the geochemical conditions representative of the Frio Formation "C" reservoir.



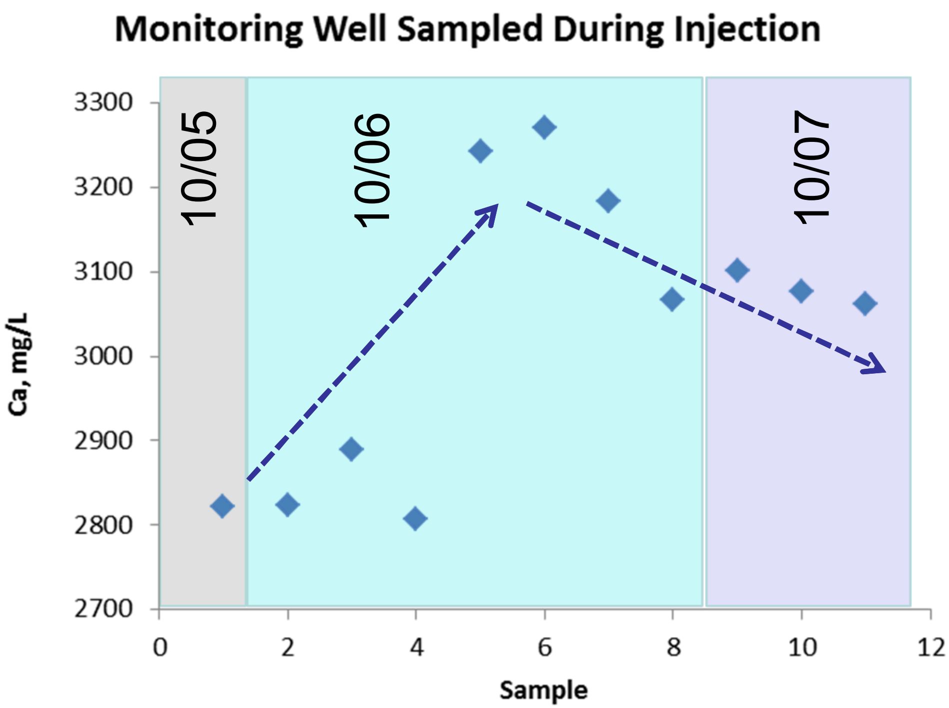
- 1-D Reactive Flow Model
- 1 m block, 23 % porosity
- Initial brine composition of Frio reservoir
- Temperature 25 °C
- Time 1000 years
- Reacting fluid – Frio brine saturated with CO_2(g): 0.82 M HCO_3^-, pH = 3.3
- Over the course of the simulation pH is allowed to rise back to 7.

Typical solids and parameters

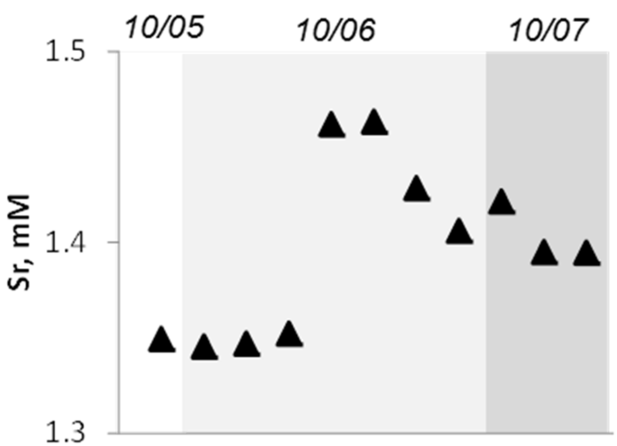
Mineral	Specific surface area cm^2/g	Kinetic rate constant mol/cm^2 sec
Calcite	9.8	$5.012 \cdot 10^{-10}$
Quartz	9.8	$1.023 \cdot 10^{-18}$
Kaolinite	151.6	$6.918 \cdot 10^{-18}$
K-feldspar	9.8	$3.89 \cdot 10^{-17}$
Albite	9.8	$1.445 \cdot 10^{-16}$

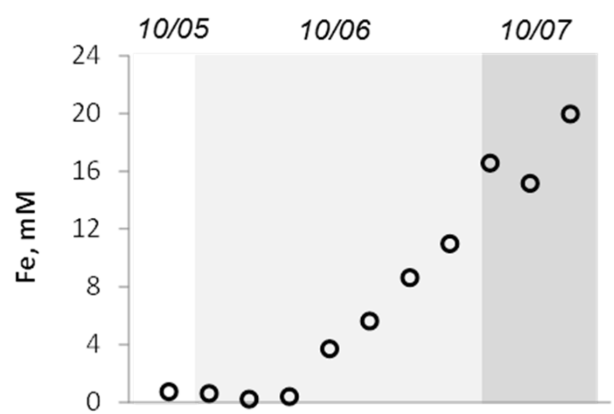
Values adapted from Xu et al., 2010, values for albite are assumed equal to oligoclase.

Results: Calcium and iron in brine samples

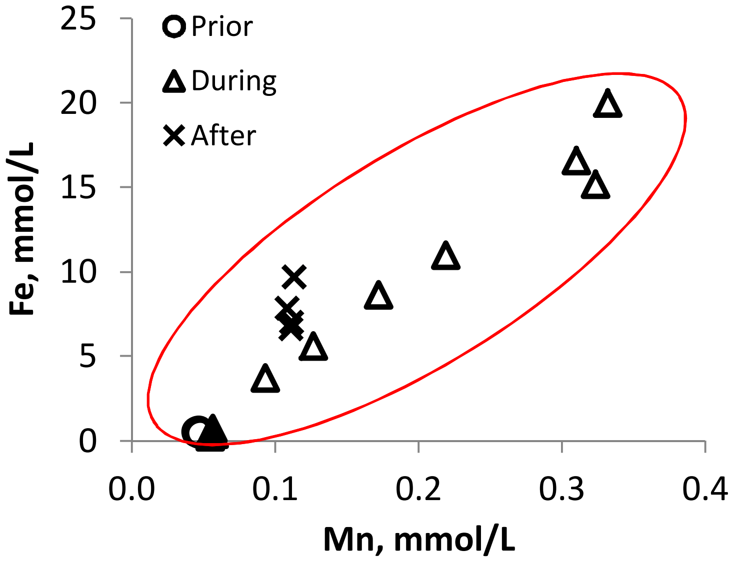


- A subset of samples collected from the monitoring well during CO_2 injection.
- Fe increases continuously.
- Ca and Sr increase, then decrease, potentially indicates full dissolution of the Ca-phase.



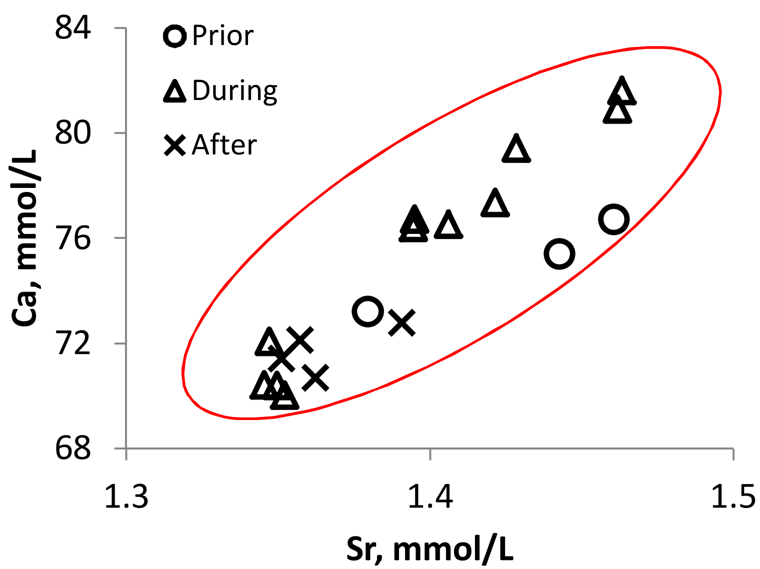


Results: Calcium and iron in brine samples



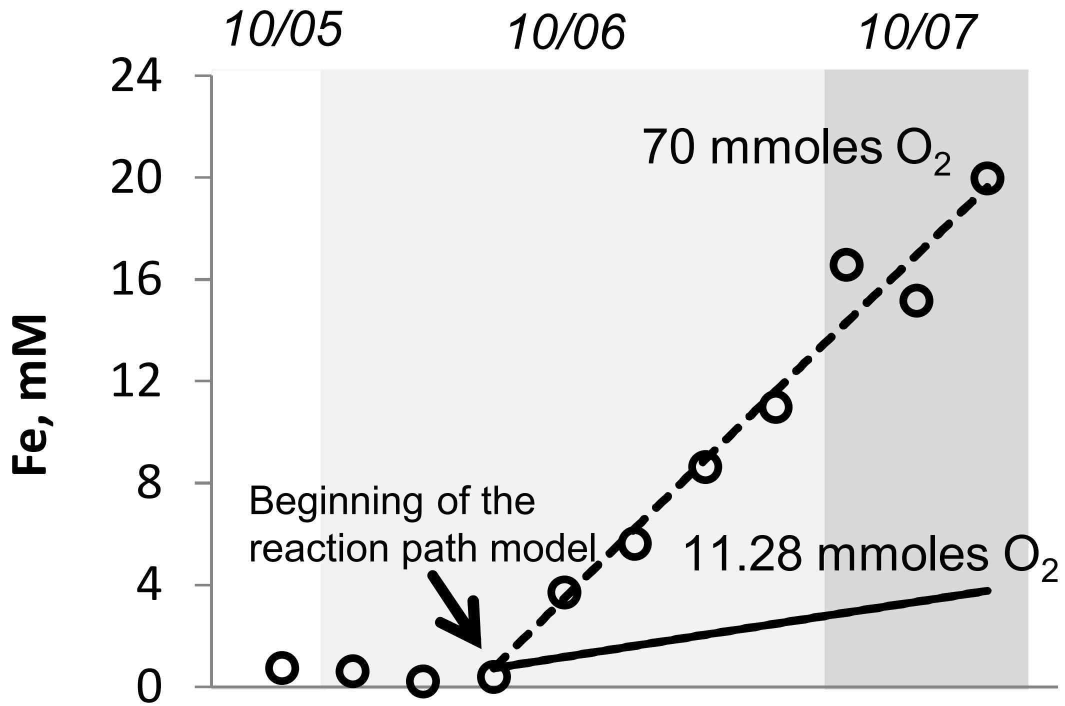
- Positive correlation - iron and manganese - indicate the same source – Mn-enriched pyrite found in the Frio "C" sandstones.
- No correlation between Fe and S – pyrite dissolution is an incongruent process.[1]

- Positive correlation - calcium and strontium - dissolution of Ca-containing mineral phase (calcite or anorthite).



[1] Descostes et al., 2004

Results: Pyrite dissolution model

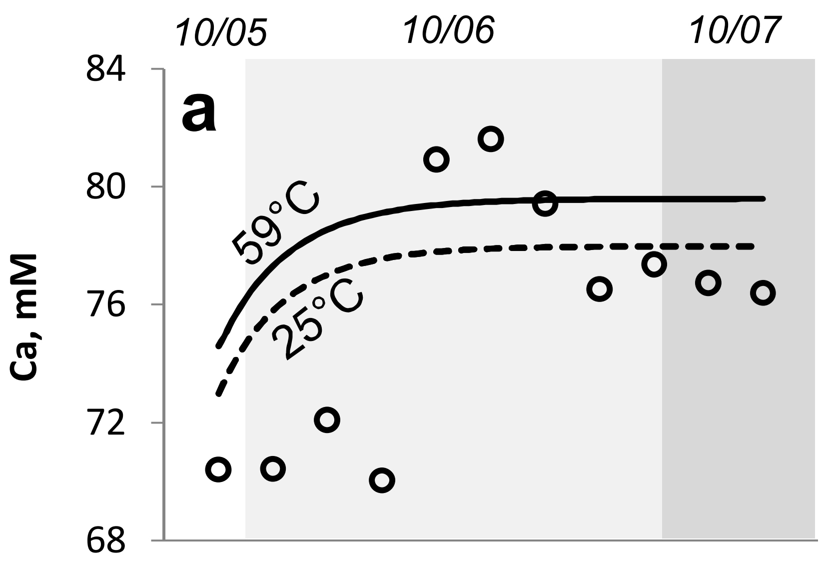


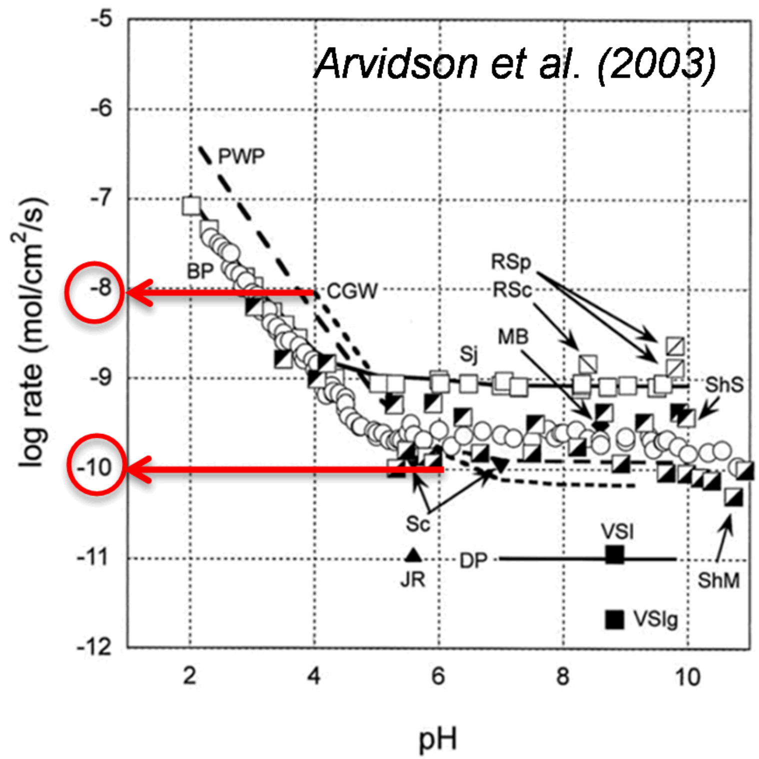
- Dissolution of pyrite by introduced O_2 – common impurity gas in CO_2 streams (3-12 vol.%). [1]
- The reaction path models were started at the onset of Fe^{2+} increase in the monitoring well samples.

- The reaction path models assume Fe is released during simple pyrite dissolution, the mass of available pyrite is set at 10 g, and temperature = 25°C.

[1] Lee et al., 2009

Results:
Calcite dissolution and associated uncertainties

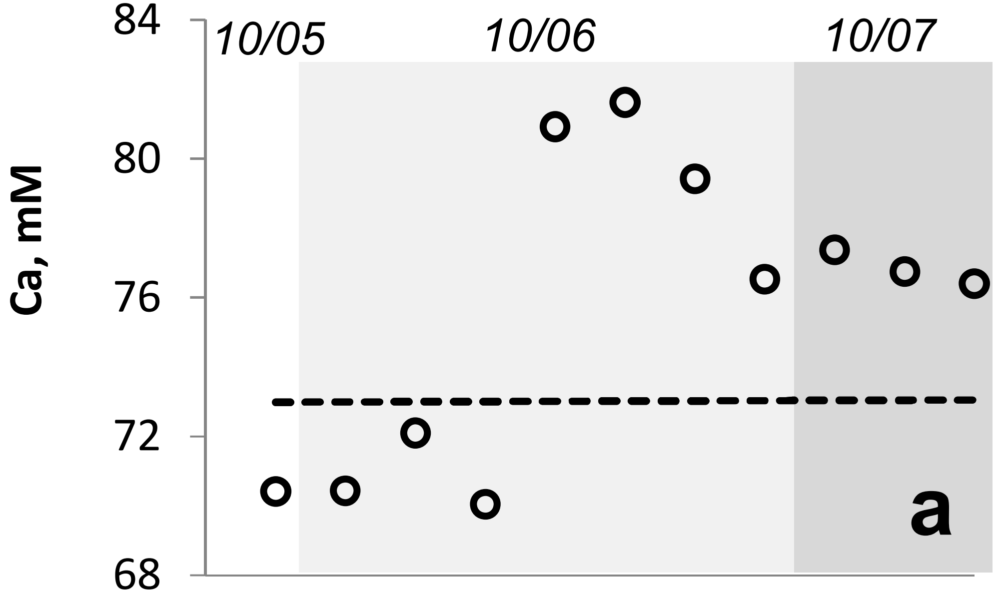




- (a) Reaction path models assume Ca is rel calcite dissolution, the mass of available c dissolution rate constant k = 10^{-8} mol cm^{-2} sec^{-1},

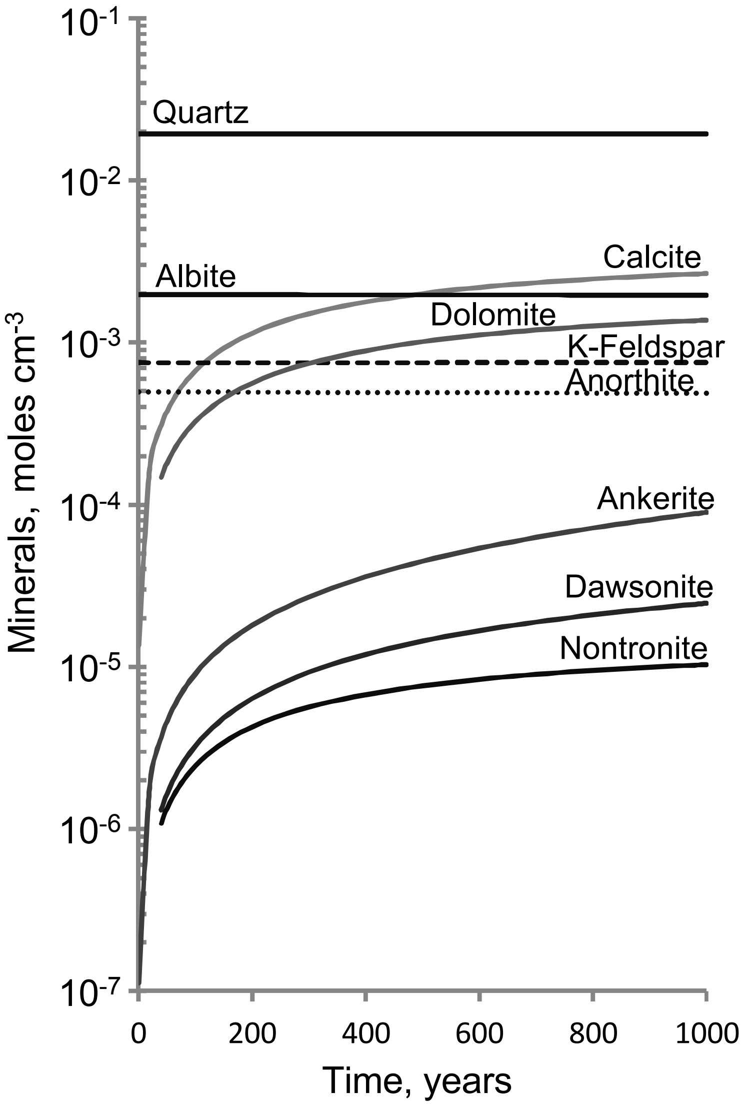
- (b) Uncertainty: dashed lines – models calculated at 25°C, solid lines – at 59°C. Group "A" = 9 g $CaCO_3$, k = 10^{-8} mol cm^{-2} sec^{-1}, group "B "- 9 g $CaCO_3$, k = 10^{-10} mol cm^{-2} sec^{-1}, group "C" – 0.09 g $CaCO_3$, k = 10^{-8} and 10^{-10} mol cm^{-2} sec^{-1}.

Results: Anorthite dissolution model

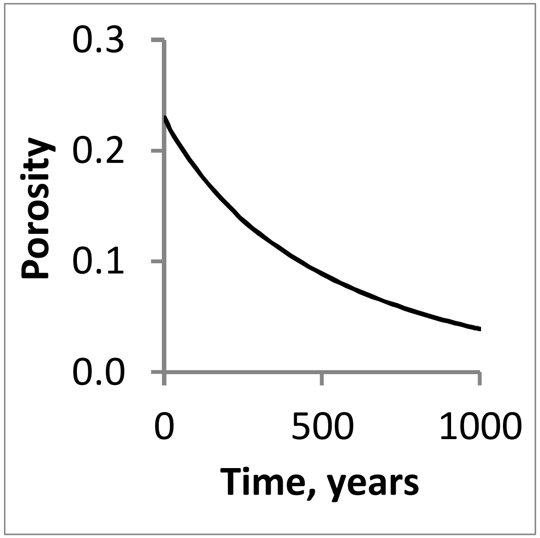


- This reaction path model assumes Ca is released during kinetically controlled anorthite dissolution.
- The mass of available anorthite was set at 35 g and at 350 g, and the calculated concentrations of dissolved calcium overlap, anorthite dissolution rate constant k = 2.1×10^{-14} mol cm^{-2} sec^{-1}, temperature is set at 25°C.

Results: Reactive flow model

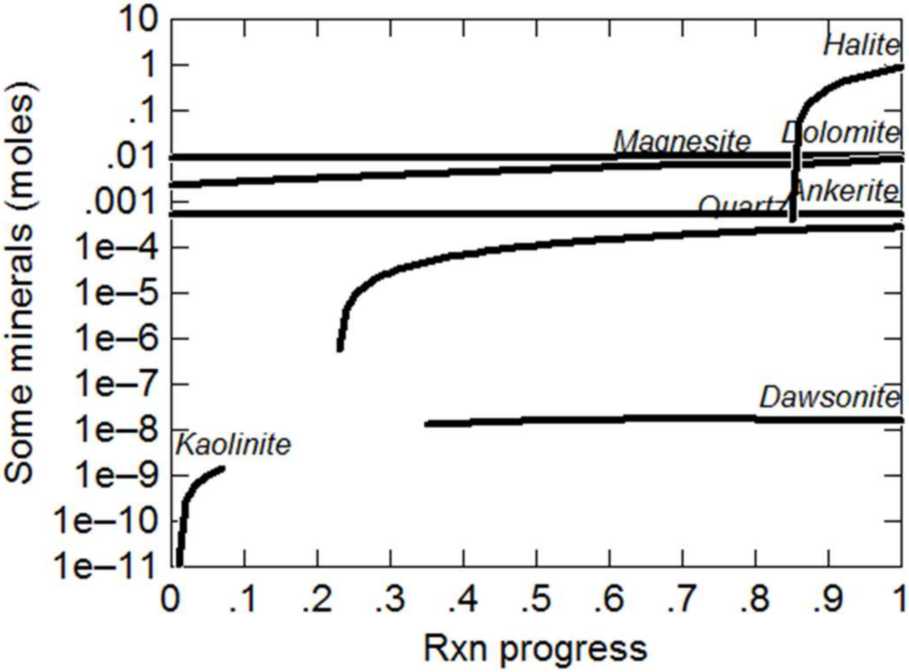


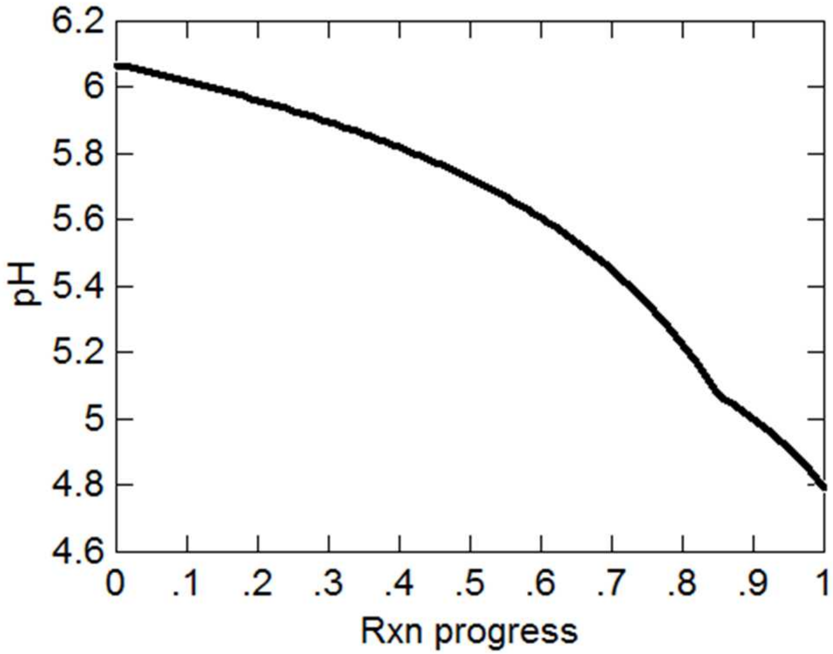
- Based on the path of reaction models, dissolution of **pyrite** and trace amounts of **calcite** are included.
- Precipitation of carbonates: dolomite, ankerite, dawsonite, and calcite, as well as smectite clay (nontronite), significant after 10 years.
- Predicted decrease in porosity: from 23 to 4%.



Precipitation due to dehydration (near wellbore)

Input: Aqueous species + Calcite. Assume brine/CO_2 did NOT equilibrate before dehydration by scCO_2. Precipitation – allowed. Single reactant -900 g H_2O





- Oversaturated minerals are allowed to precipitate before reaction;

- **Prediction**: pH decreases to **4.8**, halite, dolomite, magnesite, quartz, and dawsonite precipitate.

Calcite dissolution modeling uncertainty

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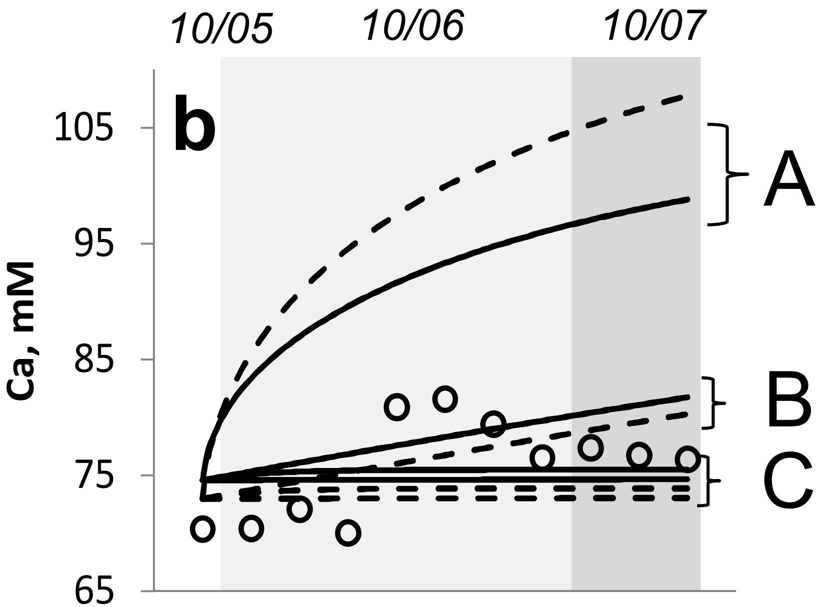
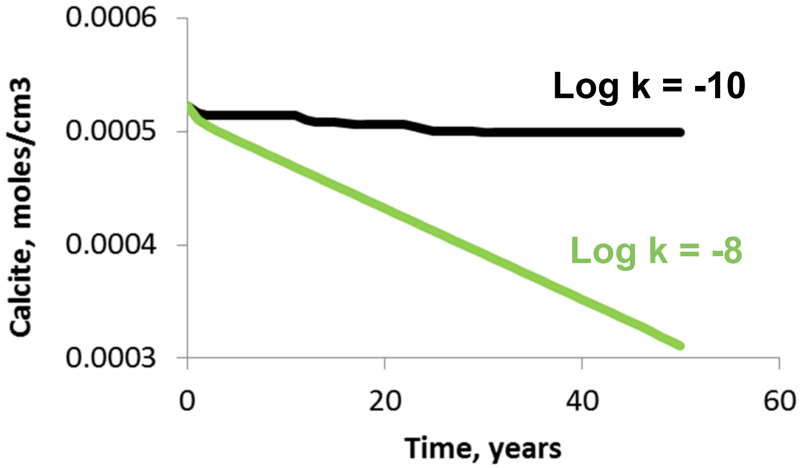
Trace amounts of calcite in the reservoir rocks:



Significant amounts of calcite in the reservoir rocks

- 2 vol. % of calcite
- Reaction with NaCl brine and dissolved CO_2, final pH 4.8.



- Calcite dissolution over 50 years differs by 60%.

Conclusions

- Increasing Ca and Sr concentrations in the monitoring well are best matched by the dissolution of **trace amounts of calcite**, whereas the dissolution kinetics of anorthite is too slow to account for the levels of observed calcium release.

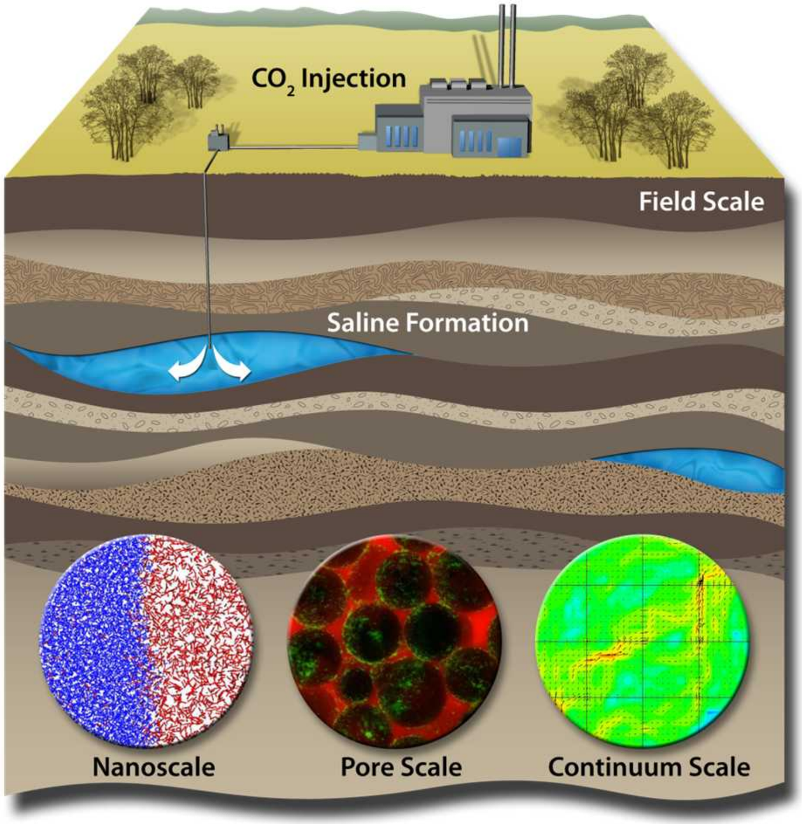
- **Pyrite** dissolution is a likely source of iron and manganese in the brine collected in the monitoring well.

- 1D reactive flow model indicates mineral precipitation in the Frio Formation "C" sandstone as the system progresses towards chemical equilibrium during a 1000 year period. Significant amounts of calcite, dolomite, ankerite, and dawsonite, as well as smectite clay (nontronite) are expected to precipitate, with a corresponding significant loss of porosity of ~19 %.

Future Work

- Laboratory experiments at pressures and temperatures typical for GCS to investigate coupled geochemical and geomechanical response of representative cap rock (shale) and brine systems during reaction with scCO2.

Overview of the Center for Frontiers of Subsurface Energy Security (CFSES)



The Energy Frontier Research Centers Aim to Accelerate Discovery Science for Energy Technologies

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- Round 1: 2009 - 2014
- CFSES is one of 2 geosciences related EFRC
- Renewal started 08/2014
- 4 year program
- **CFSES is one of 3 geosciences related EFRCs**

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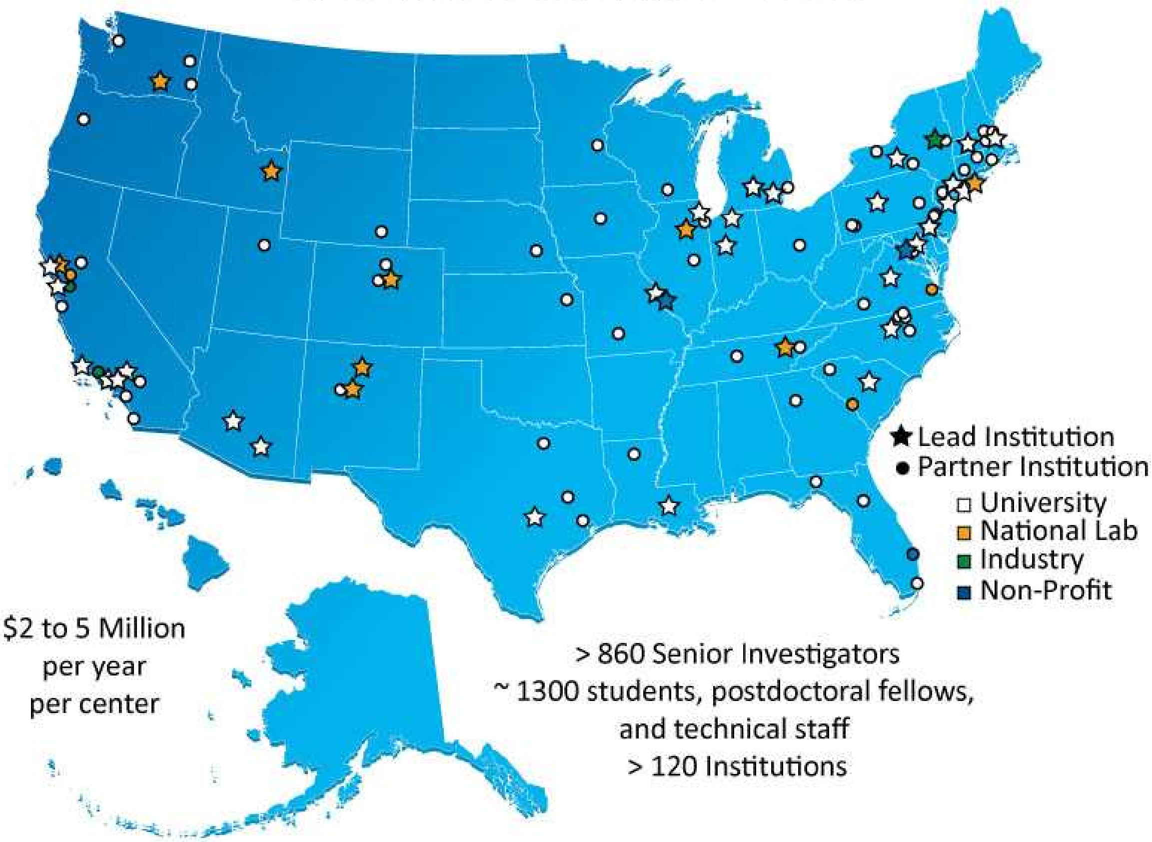
~~46~~ EFRCs in 35 States + D.C.



Ensure Safe Storage of CO_2

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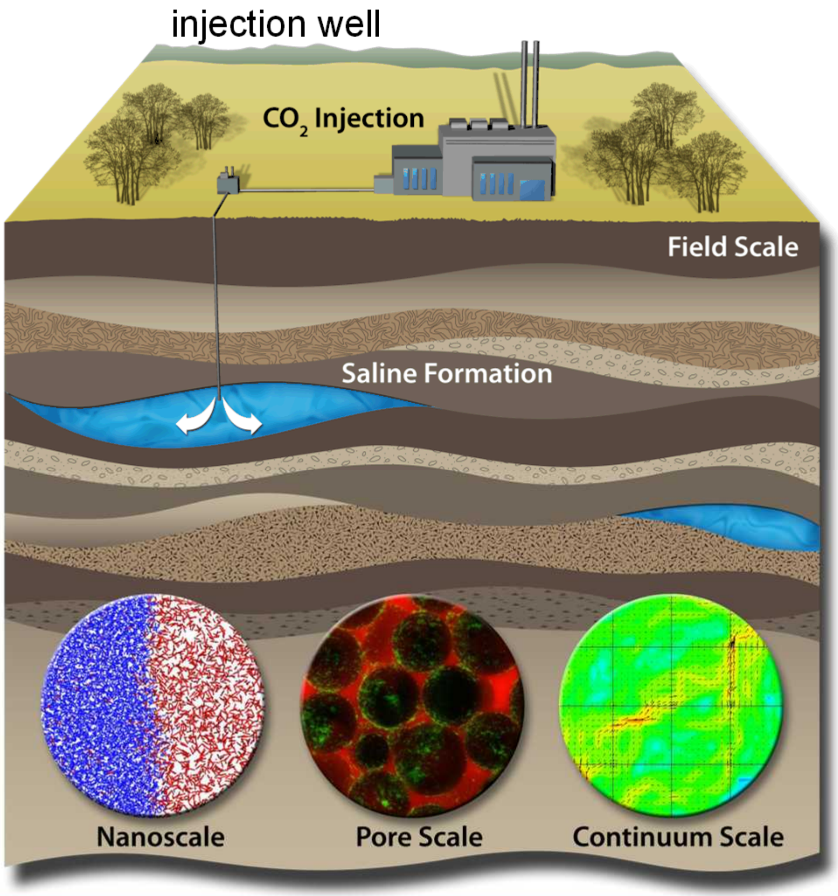
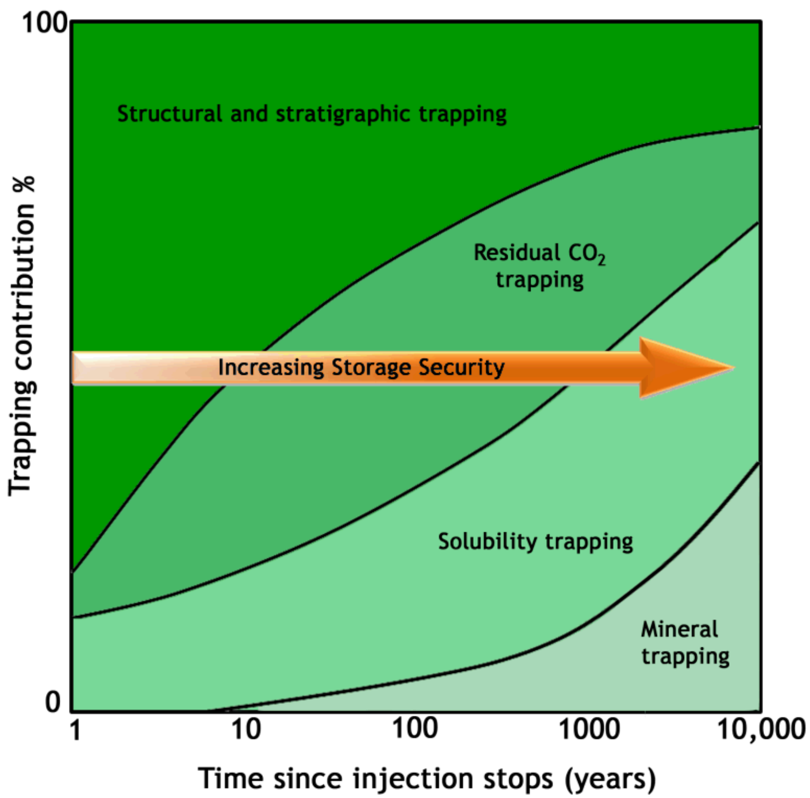
The Center for Frontiers of Subsurface Energy Security (CFSES) is pursuing scientific understanding of multi-scale, multi-physics processes to ensure safe and economically feasible storage of carbon dioxide and other byproducts of energy production without harming the environment.

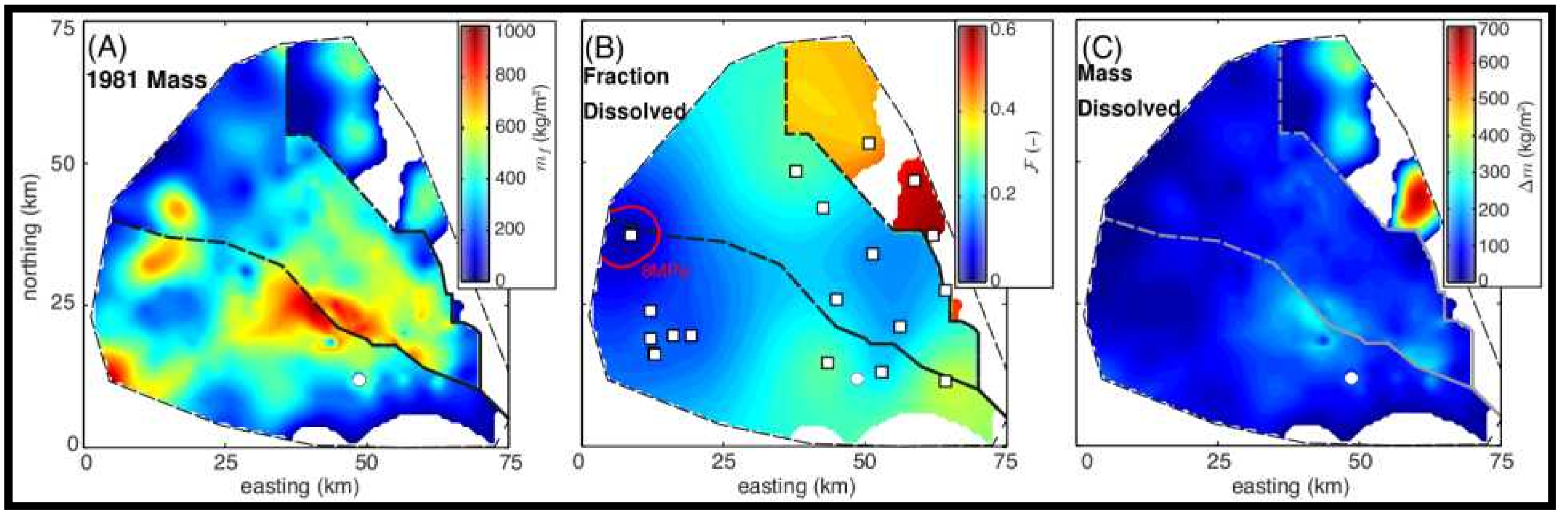




Natural analogs: long-term dissolution of stored CO_2

Storing gigatons of CO_2 in deep saline aquifers in a few decades represents a substantial disequilibration of the subsurface environment. Because the CO_2 phase is buoyant but brine becomes more dense when saturated with dissolved CO_2, a central question for GCS security is the rate of dissolution of a CO_2 plume after it has been emplaced.

The Bravo Dome reservoir demonstrates that long-term, safe geological CO_2 storage is possible.



A) Mass of CO_2 per unit area in the Bravo Dome reservoir in 1981.

B) Map of the local fraction of CO_2 dissolved.

C) Map of the local change in the mass of CO_2 per unit area.

- **Estimated 22% of the emplaced CO_2 has dissolved into the brine over 1.2 My. Estimated a convective dissolution rate of 0.1 g/(m^2y)**

Martinez and Hesse, In Preparation; Sathaye et al., 2014

How Important is CO_2 Dissolution?

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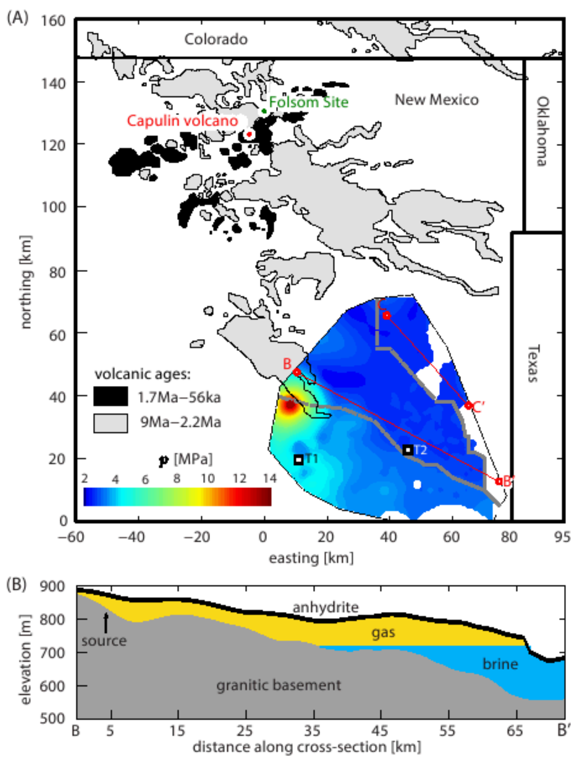
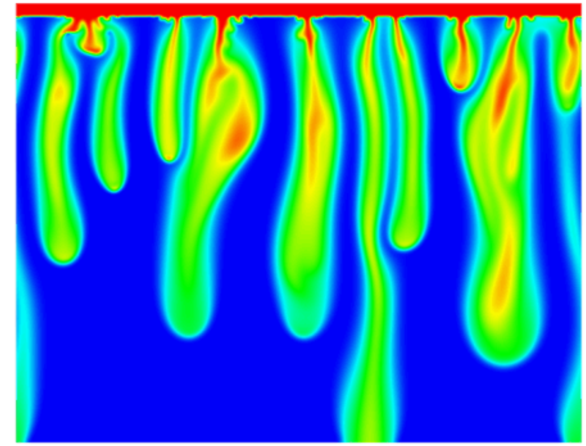
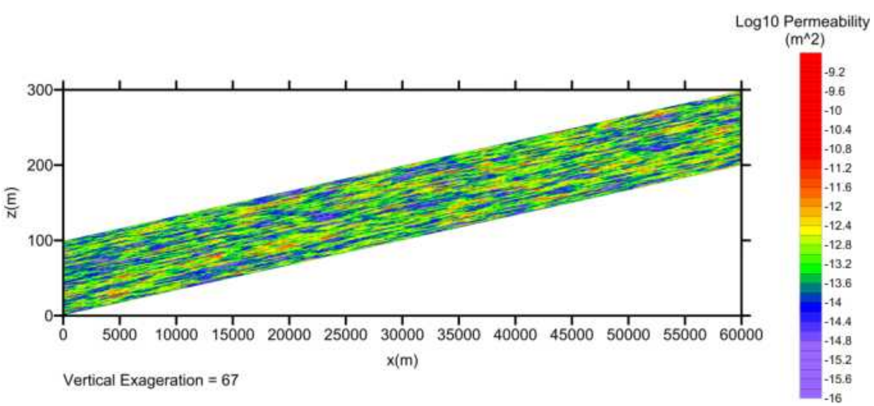
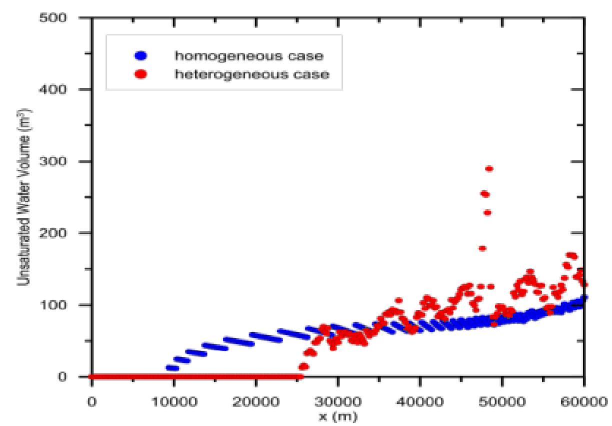


- Bravo Dome Site: 360Mt CO_2 dissolved over 1.5Ma.
- Convectively driven dissolution flux may be roughly 3x larger than current estimates.



<u>Goal</u>: Improved estimates of the long-term dissolution rate of CO_2 into brine by including the two-phase region above the gas-water contact in model simulations. Long-term dissolution rate can be enhanced by greater than 3 times the dissolution rates derived from ignoring the capillary transition zone.





Dissolution is enhanced by heterogeneity.

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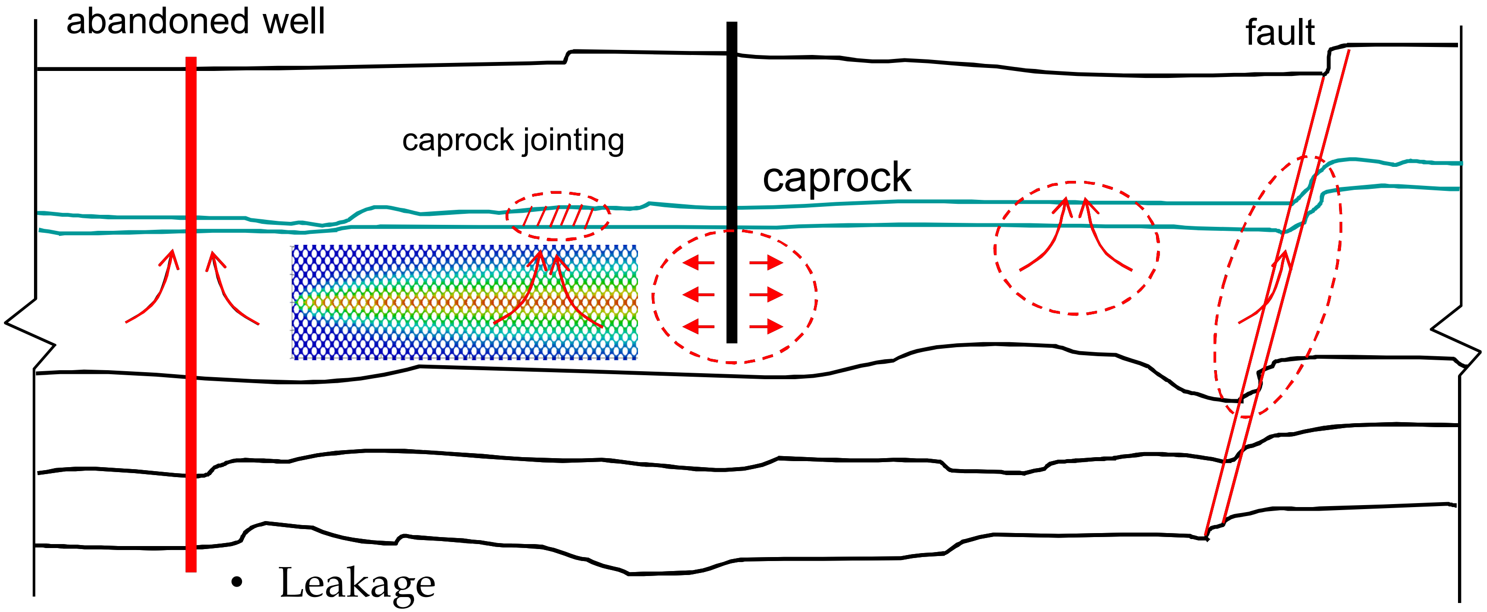
CFSES will pursue scientific advances to understand chemico-mechanical coupling between supercritical CO_2 and clay minerals, understand and predict modes and fluxes of reactive CO_2 migration, and design, develop and apply novel materials that will alter fluid-assisted perturbations in heterogeneous geomaterials.



- Leakage
  - Wellbores
  - Faults
- Injection induced damage
- Brine migration to overlying aquifers
- Induced seismicity

Integrating Research Themes with Challenges

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	Challenge 1: Sustaining large storage rates	Challenge 2: Using pore space with unprecedented efficiency	Challenge 3: Controlling undesired or unexpected behavior
Theme 1: Fluid-Assisted Geomechanics	• Single Fracture propagation and cohesive zone modeling • Phase-field modeling	• Single Fracture propagation and cohesive zone modeling	• Bulk rock strengthening/weakenin g evaluation
Theme 2: Multifluid Geochemistry	• Caprock chemical and mechanical stability	• Bravo Dome brine-gas mass transfer • Chemistry at the fluid-fluid interface	• Caprock chemical and mechanical stability • Reactions of CO_2 with clay minerals
Theme 3: Buoyancy-Driven Multiphase Flow	• Meter-scale experiments • Core-scale X-ray CT experiments	• Meter-scale experiments • Core-scale X-ray CT experiments • Mesoscale modeling and invasion-percolation modeling • Ganglion dynamics modeling	• Nanoparticle experiments

Center For Frontiers of Subsurface Energy Organizational Structure

Sandia National Laboratories

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THEME 3: BUOYANCY-DRIVEN MULTIPHASE FLOW

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