SAND2015-2492PE

# Mineral Dissolution and Precipitation in Rock-Brine-$CO_2$ Systems: Geochemical Modeling and Experiments

## $CO_2$ Injection at the Frio-I Brine Pilot: Geochemical Modeling

Anastasia Ilgen and Randall Cygan

### Frio-I Pilot in 2004

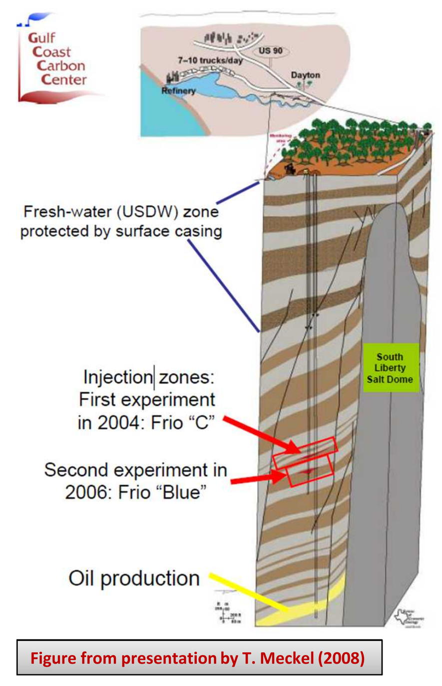
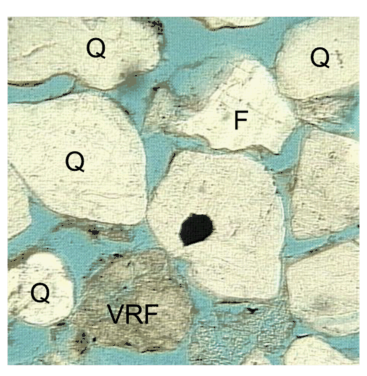


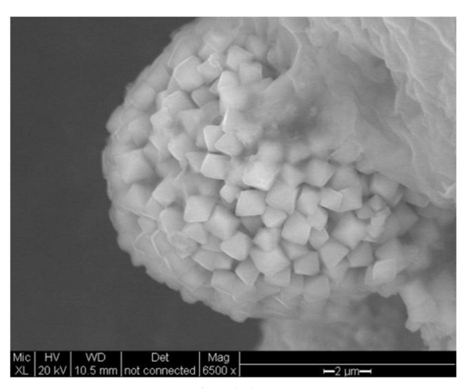
Figure from presentation by T. Meckel (2008)

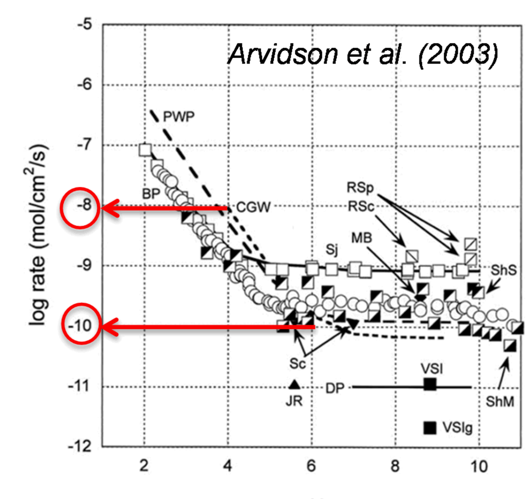
- Setting: salt dome flank, Frio sandstone;
- 1600 tons at 3 kg/s, 10 day injection in 1545 m deep well;
- ~ 40 water samples collected (1530 m deep monitoring well).

Petrographic observations

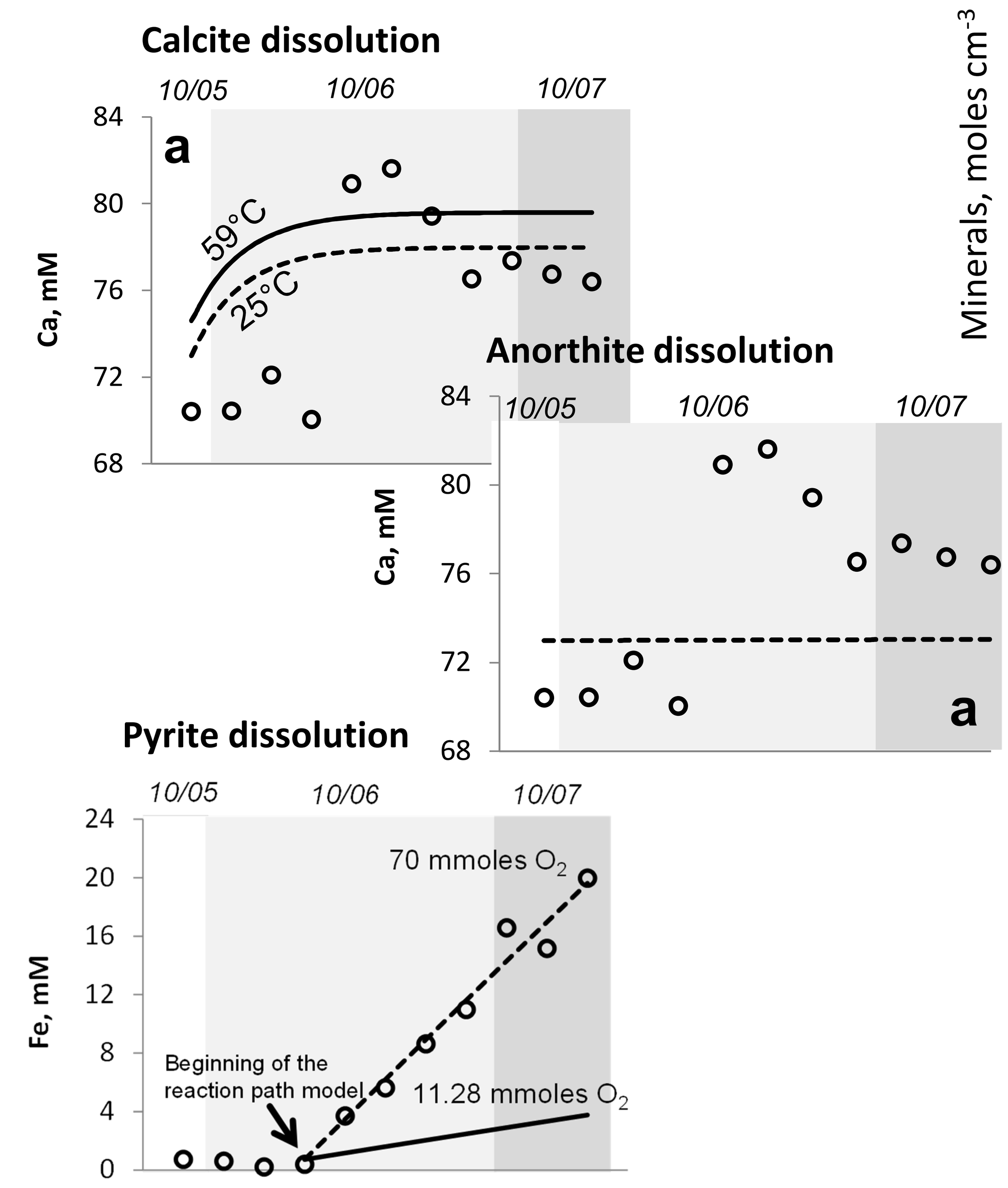
- Frio Formation "C" sandstone contains 24 wt. % of feldspar, mostly **anorthite** $CaAl_2Si_2O_8$.
- No crystalline iron oxyhydroxides.[23]
- Calcite cement in Frio Formation varies and can be absent.
- Petrographic study of the Upper Frio Formation "C" found no calcite cement.
- Abundant fine-crystalline **pyrite** $FeS_2$.[23]

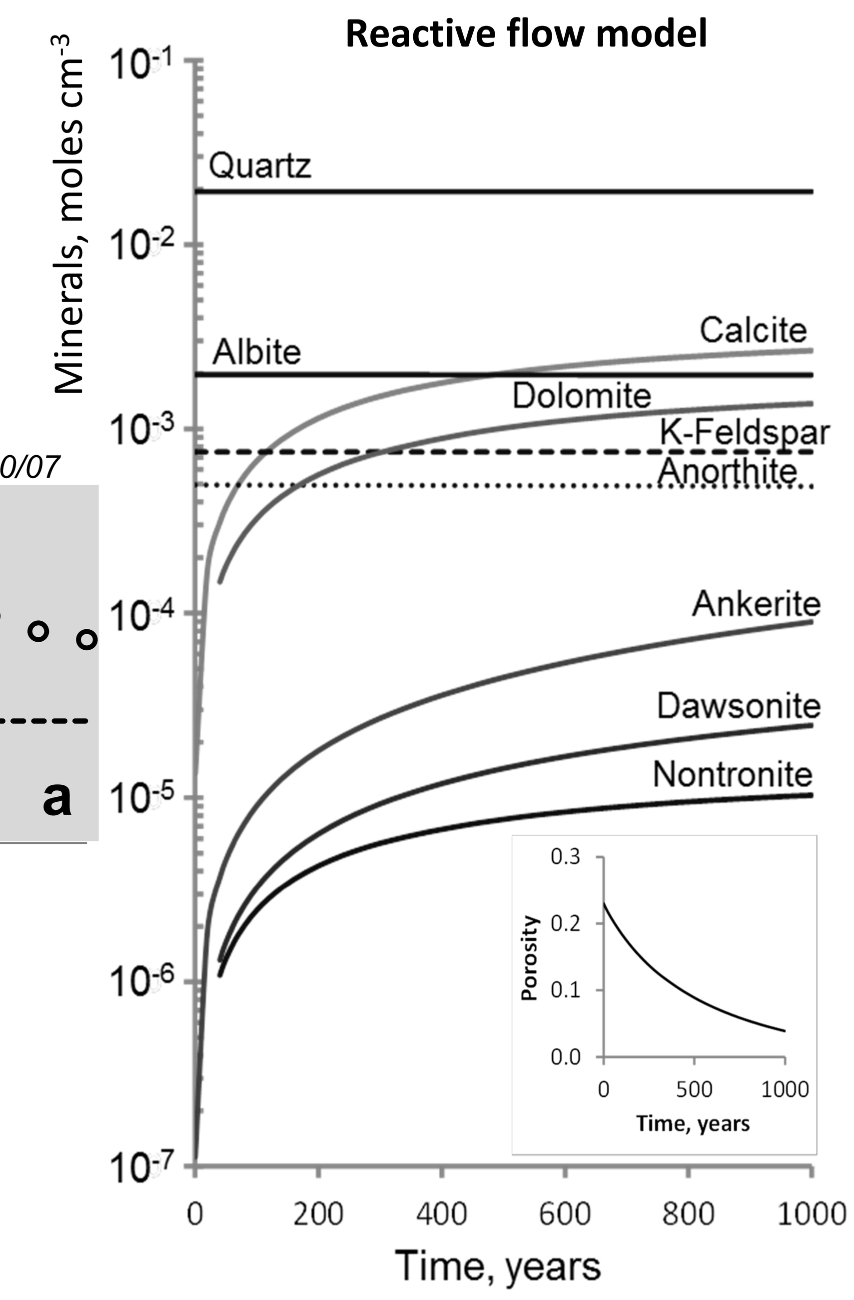

Quartz (Q), feldspar (F), and volcanic rock fragments (VRF)


Framboidal pyrite




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




### Objectives

- Hypothesis : increase in **iron** is due to the **dissolution of pyrite**; and increase in **calcium** - to the **dissolution of anorthite**.
- 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.
- Path of reaction and reactive transport modeling using Geochemists Work Bench (Bethke, 1998).

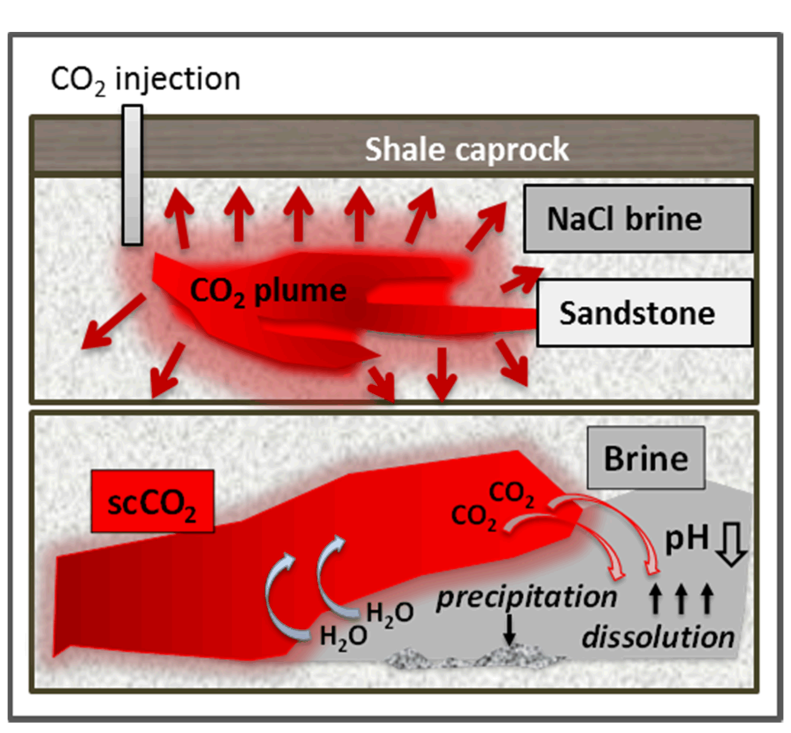
### Conclusions

- 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 %.

## Alteration of Mancos Shale by $CO_2$-charged Brine

Anastasia Ilgen, Thomas Stewart, and Thomas Dewers

### Geochemical response triggered by the injection of $CO_2$




- Supercritical $CO_2$ stimulates **geochemical responses**: acidification of parent brine, and dehydration of mineral surfaces by the dispersing sc$CO_2$ phase.[1-3, 8]
- Experimental and field studies: geochemical reactions differ significantly for different rock assemblages and brine compositions.[7-9]
- Typical low-permeability shale cap rocks 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]

### Goal

Laboratory experiments at pressures and temperatures typical for GCS to understand time-dependent chemo-mechanical coupling in heterogeneous caprock, and identify chemical mechanisms controlling sub-critical fracture.

### Experimental Program Objectives

- Dissolution rates for **feldspars**, **carbonates**, and **clay minerals** at reservoir conditions (sc $CO_2$, brine, high pressure and temperature)
- Evolution of clay and carbonate mineralogy in sc $CO_2$-brine-caprock systems
- Nano-scale weakening of shale lithofacies as a result of shale alteration by $CO_2$-brine
- Redox reactions driven by impurity gases ($O_2$, NOx, and SOx), and their feedback to coupled chemical-mechanical caprock response

### Experiments with shale caprock

| Alteration at **low** p $CO_2$ | Alteration at **high** p $CO_2$ | Nano-pillar indentation |
|---|---|---|
| Mineral dissolution kinetics at conditions representative of the diffuse part of the $CO_2$ plume in contact with shale caprock. | Mineral dissolution kinetics, at conditions where supercritical $CO_2$ and brine coexist and are in contact with shale caprock. | Comparing the unaltered and $CO_2$-brine-altered shale: deformation modes, contact hardness, resistance to plastic deformation, time constants for time-dependent deformation, and the fracture resistance. |

### Alteration Experiments

**Low p $CO_2$**


- Stirred reactor pressurized with $CO_2$
- Powdered shale + brine

**High p $CO_2$**


- Flexible bags in a rocking autoclave.
- Powdered shale or shale chips + brine + sc $CO_2$

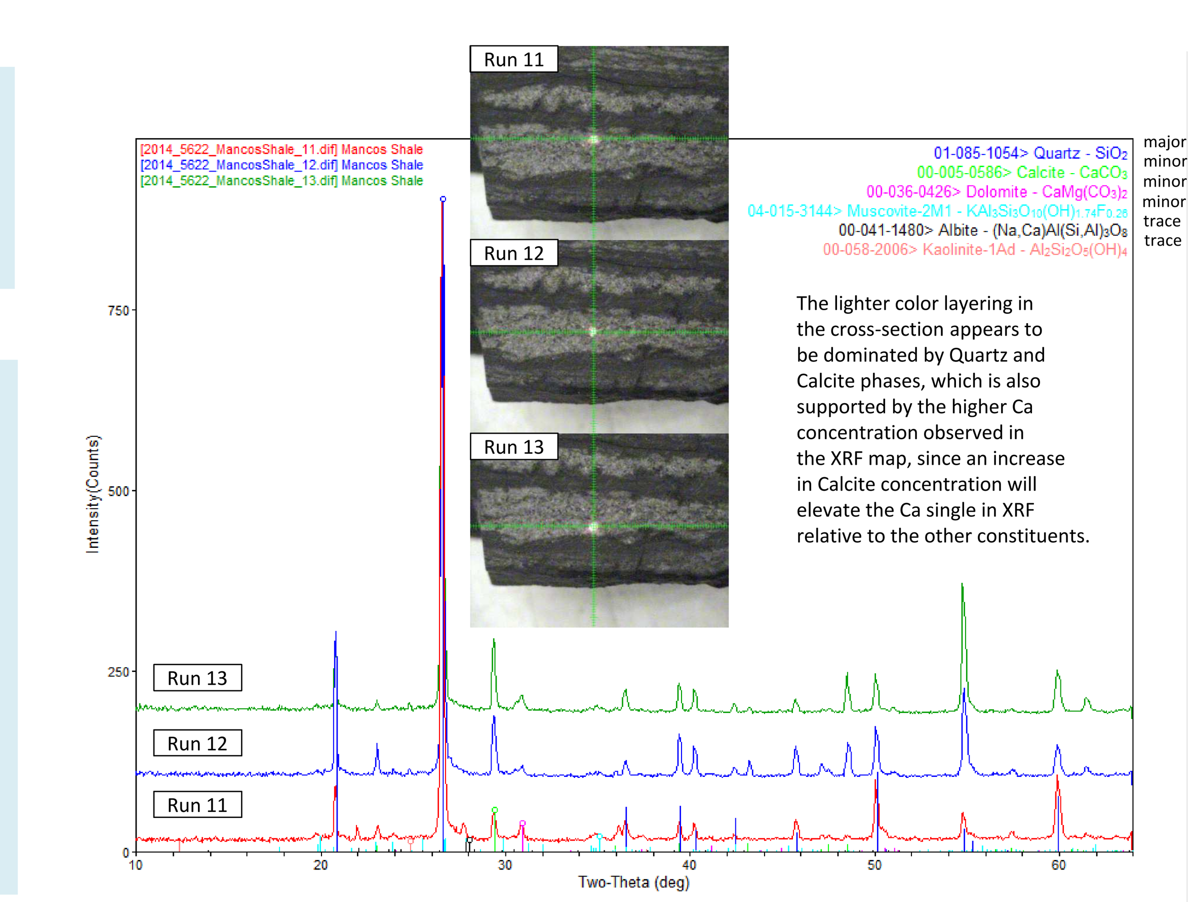
### Mancos shale

**Bulk mineralogy**

Quartz, calcite, dolomite, muscovite, pyrite, hematite, albite, kaolinite

**Synthetic brine composition**

| | |
|---|---|
| pH | 7.44 |
| $Cl^-$, mg/L | 1589 |
| $NO_3^-$, mg/L | 4.1 |
| $SO_4^{2-}$, mg/L | 47251 |
| $Fe^{2+}$, mg/L | 2 |
| $Ca^{2+}$, mg/L | 484 |
| $Na^+$, mg/L | 19000 |
| $Mg^{2+}$, mg/L | 2700 |
| $K^+$, mg/L | 20.5 |




This material is based upon work supported as part of the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001114. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.