

Shale-brine-CO₂ interactions and the long-term stability of shale caprock

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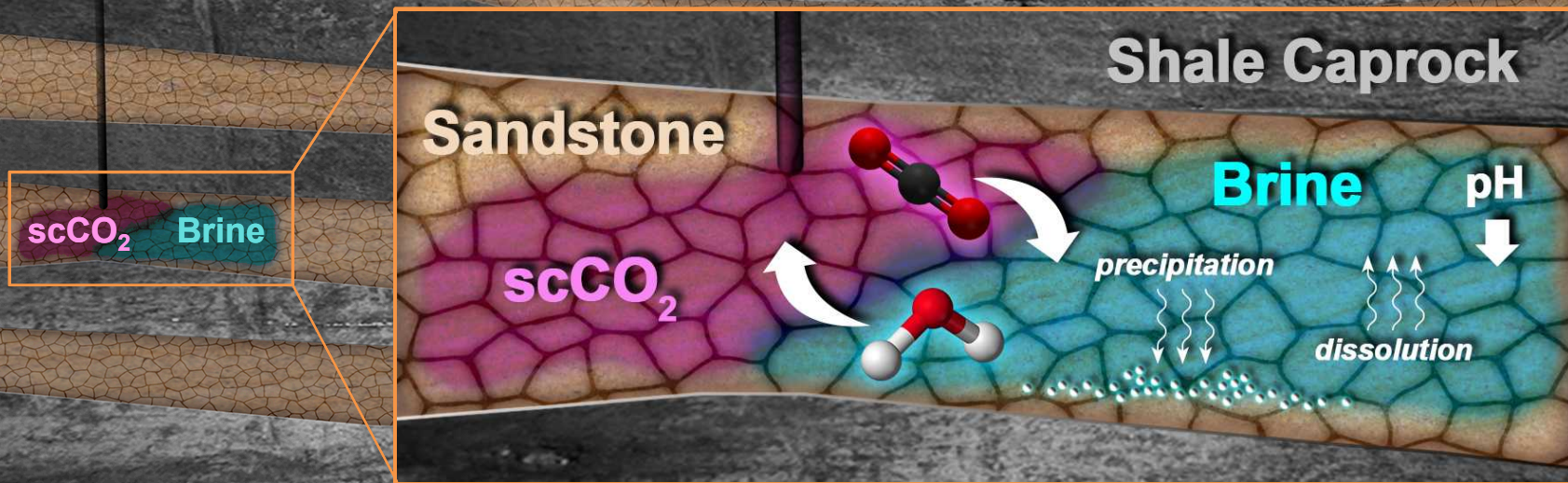
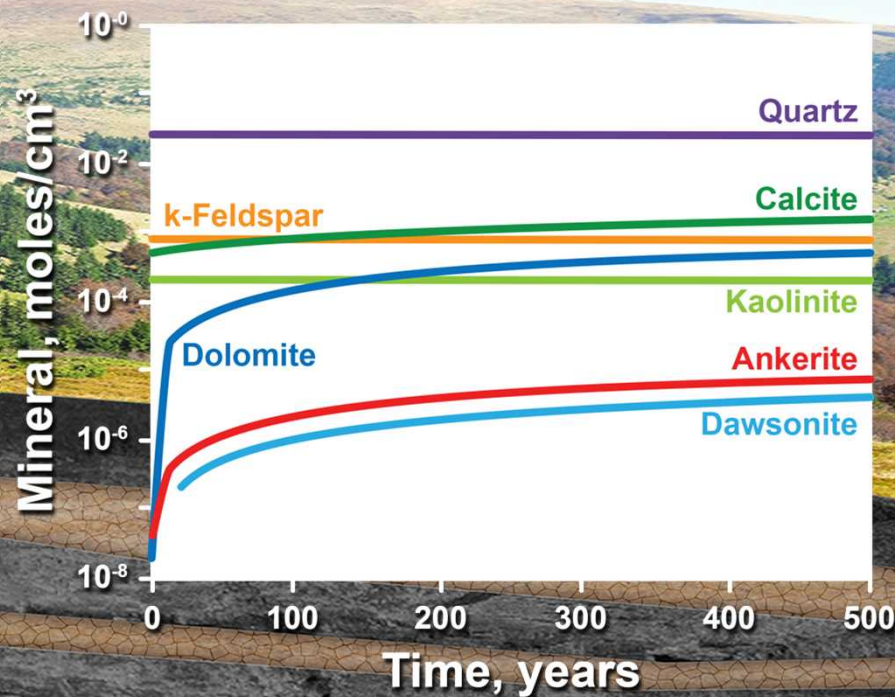
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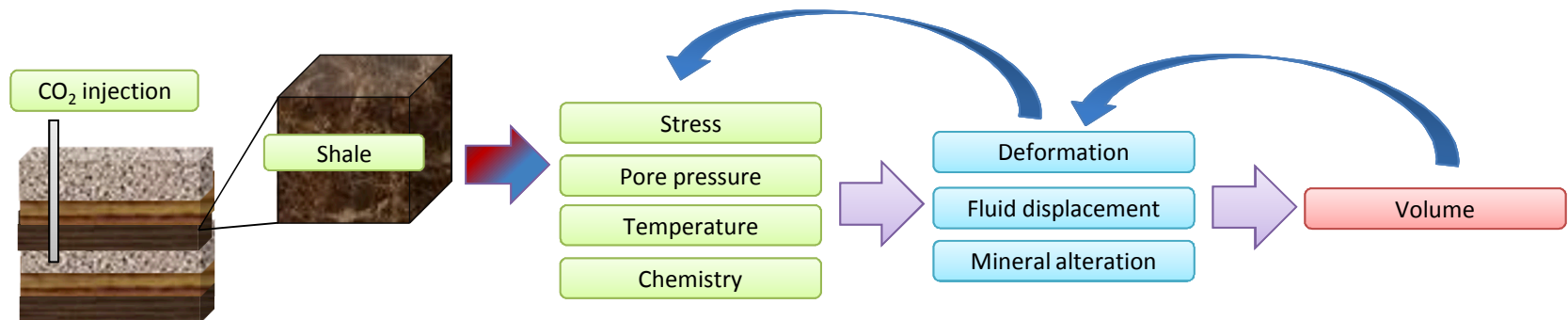
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CO₂ injection



Geochemical response triggered by the injection of CO₂

- At geologic storage PT: CO₂ is supercritical (scCO₂).
- scCO₂ stimulates **geochemical responses**: acidification of parent brine, and dehydration of mineral surfaces.^{1-3, 8}
- Experimental and field studies: geochemical reactions differ significantly for different rock assemblages and brine compositions.⁷⁻⁹
- Low-permeability caprocks (shale) are reactive at the higher end of the geologic carbon storage temperature range.^{10, 11}
- Dissolution and secondary mineral precipitation control the evolution of **porosity** and **permeability**⁸, with potential impact on the caprock integrity, and CO₂ 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

Coupled chemo-mechanical processes in shale caprock

•Objectives of this activity

–Establish quantitative relationships between chemical reactions triggered by the addition of supercritical CO₂ and changes in nano- to micro-scale mechanical properties of shale.

•Team & Roles

- Anastasia Ilgen: shale characterization, alteration, and geochemical modeling
- Tom Stewart: alteration experiments
- Josh Feldman: alteration experiments
- Jon Major: Crystal Geyser field study, geomechanical experiments
- Peter Eichhubl: Crystal Geyser field study, geomechanical experiments
- Michael Aman: micromechanical characterization, scratch and indentation
- Nicolas Espinoza: micromechanical characterization, scratch and indentation
- Charles Choens: micromechanical characterization, micro-pillar indentation
- Tom Dewers: micromechanical characterization, micro-pillar indentation
- Pania Newell: modeling



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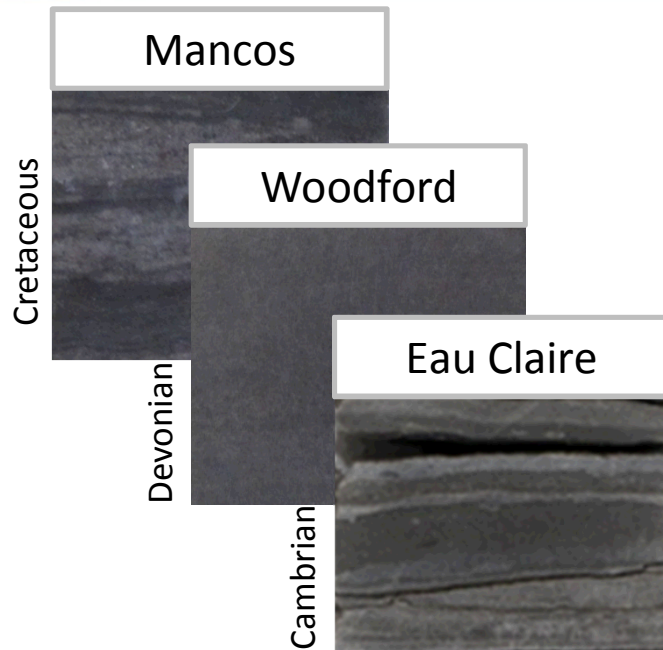


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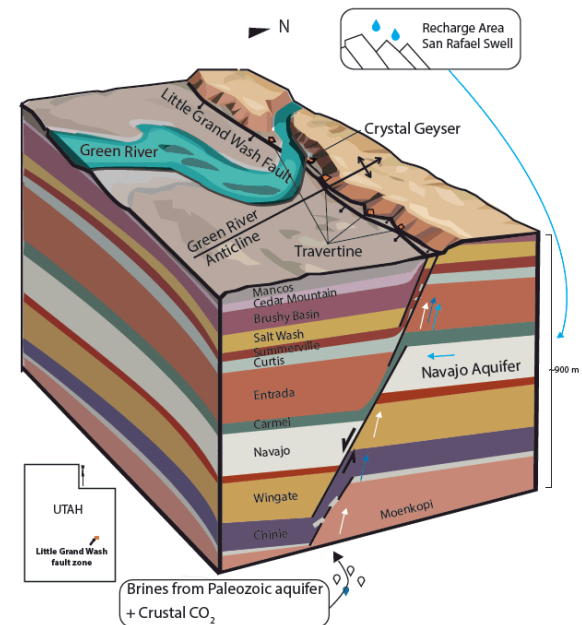
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Coupled chemo-mechanical processes in shale caprock



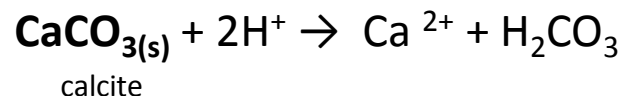
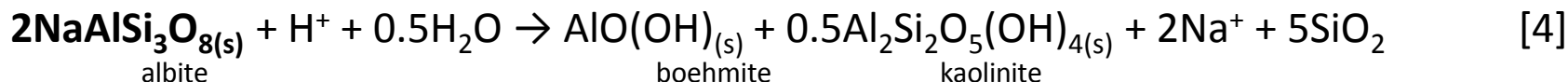
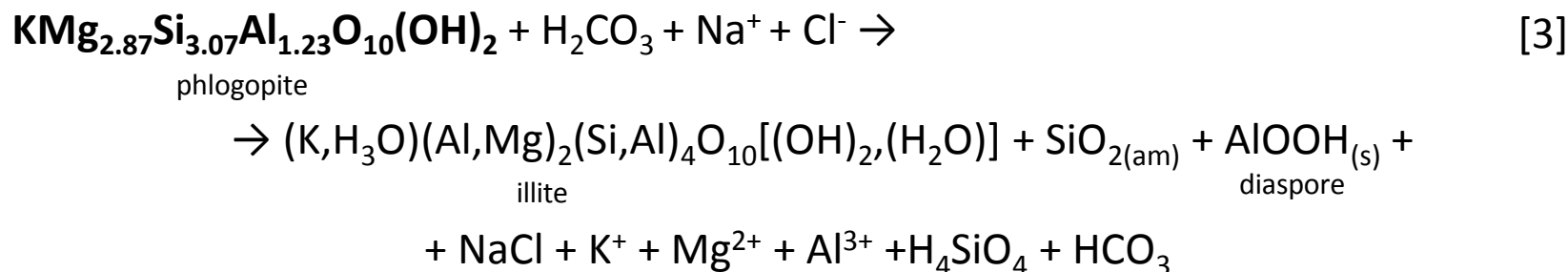
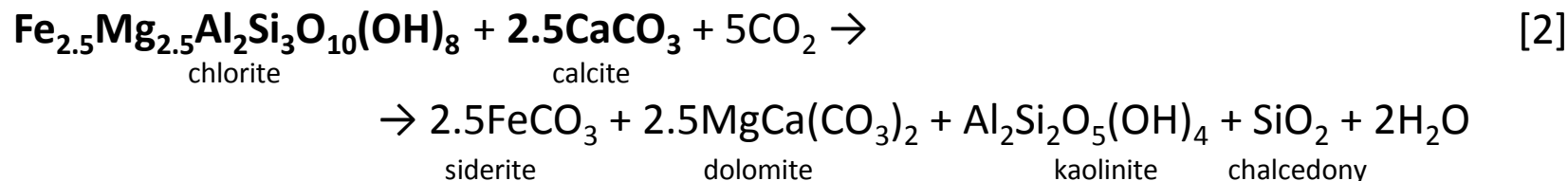
- **Laboratory experiments** on shale samples at conditions typical of GCS to understand time-dependent geochemical reactions.
- Geochemical modeling for data interpretation.
- Nano- and micro-mechanical characterization to understand chemical effects on mechanical properties in heterogeneous shale caprock.

- **Field Study** on shale and sandstone to understand fractures in natural CO₂ reservoir caprock: Crystal Geyser analog site.
- Mechanical characterization to understand chemical effects on mechanical properties in shale caprock.



Mineral alteration

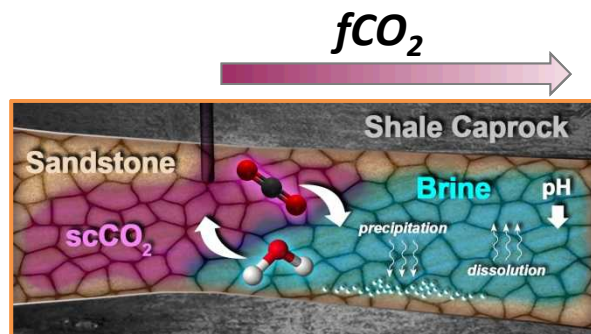
- Dissolution of **feldspars** and **phyllosilicate minerals**, dissolution and re-precipitation of **carbonate** and **clay minerals** [1].



-
- [1] Liu et al., 2012
 [2] Gaus et al., 2010
 [3] Garcia et al., 2012
 [4] Fu et al., 2009



Shale alteration in brine-CO₂ mixtures



- Stirred reactors pressurized with **CO₂**
- Control reactors – **N₂** or ambient atm
- Powdered shale ($A_{\text{BET}} = 8.3 \text{ m}^2 \text{ g}^{-1}$) + **brine**
- Sample brine and solids at time intervals
- Analysis by IC, ICP-MS, and XRD
- Geochemical modeling

Shale alteration in brine-CO₂ mixtures

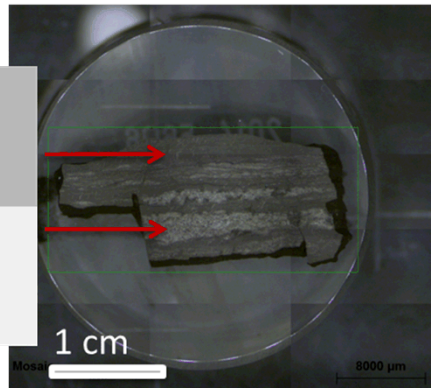
Mancos

Synthetic brine*

pH	7.44	I = 1.45 M
Cl ⁻	1589	mg/L
NO ₃ ⁻	4.1	mg/L
SO ₄ ²⁻	47251	mg/L
K ⁺	20.5	mg/L
Ca ²⁺	484	mg/L
Na ⁺	19000	mg/L
Mg ²⁺	2700	mg/L
Fe ²⁺	2	mg/L

Quartz, Calcite,
Dolomite, Muscovite
Albite
Pyrite, Hematite

Quartz, Calcite,
Dolomite, Muscovite
Albite
Kaolinite



Woodford



Synthetic brine**

pH	6.5	I = 0.26 M
Cl ⁻	8651	mg/L
HCO ₃ ⁻	1100	mg/L
SO ₄ ²⁻	82	mg/L
Ca ²⁺	65	mg/L
Na ⁺	5910	mg/L
Mg ²⁺	20	mg/L

Estimated solubility of CO₂ in brine = 0.84 M**

* Developed based on the dataset from "Natural Contamination from the Mancos Shale" Report, US DOE, ESL-RPT-2011-01.

** Using Duan and Sun (2003) data for NaCl.

* *Developed based on U.S. Geological Survey National Produced Waters Geochemical Database v2.1, Woodford shale



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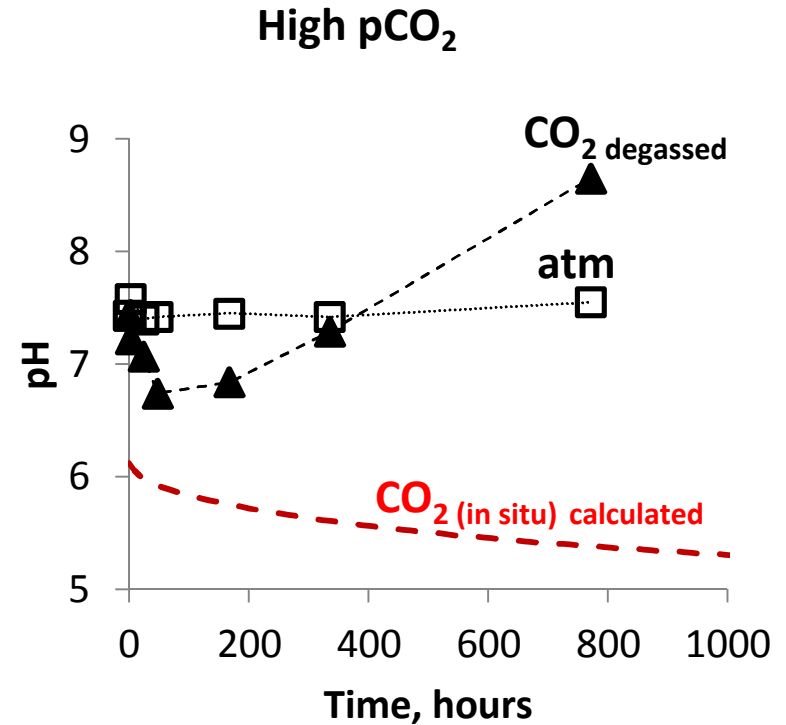
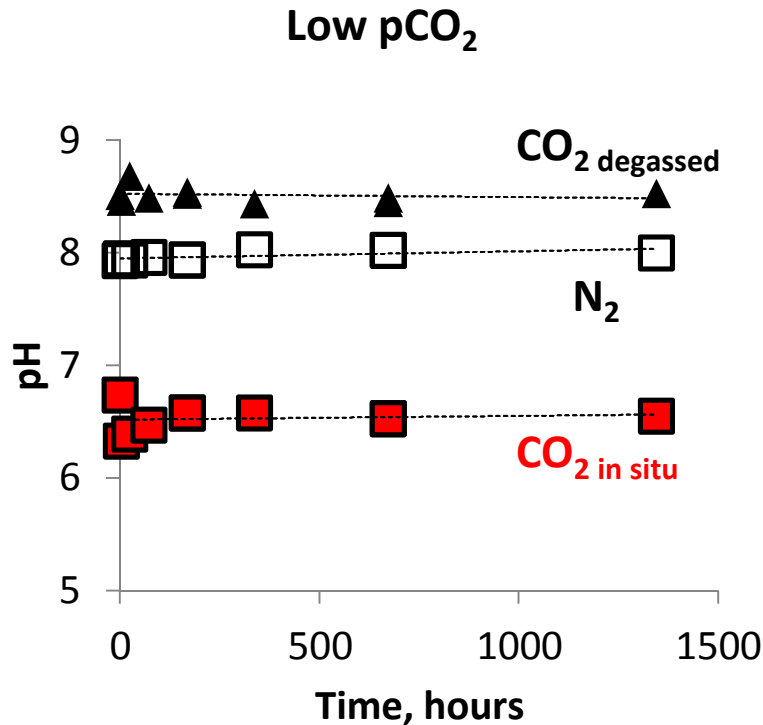


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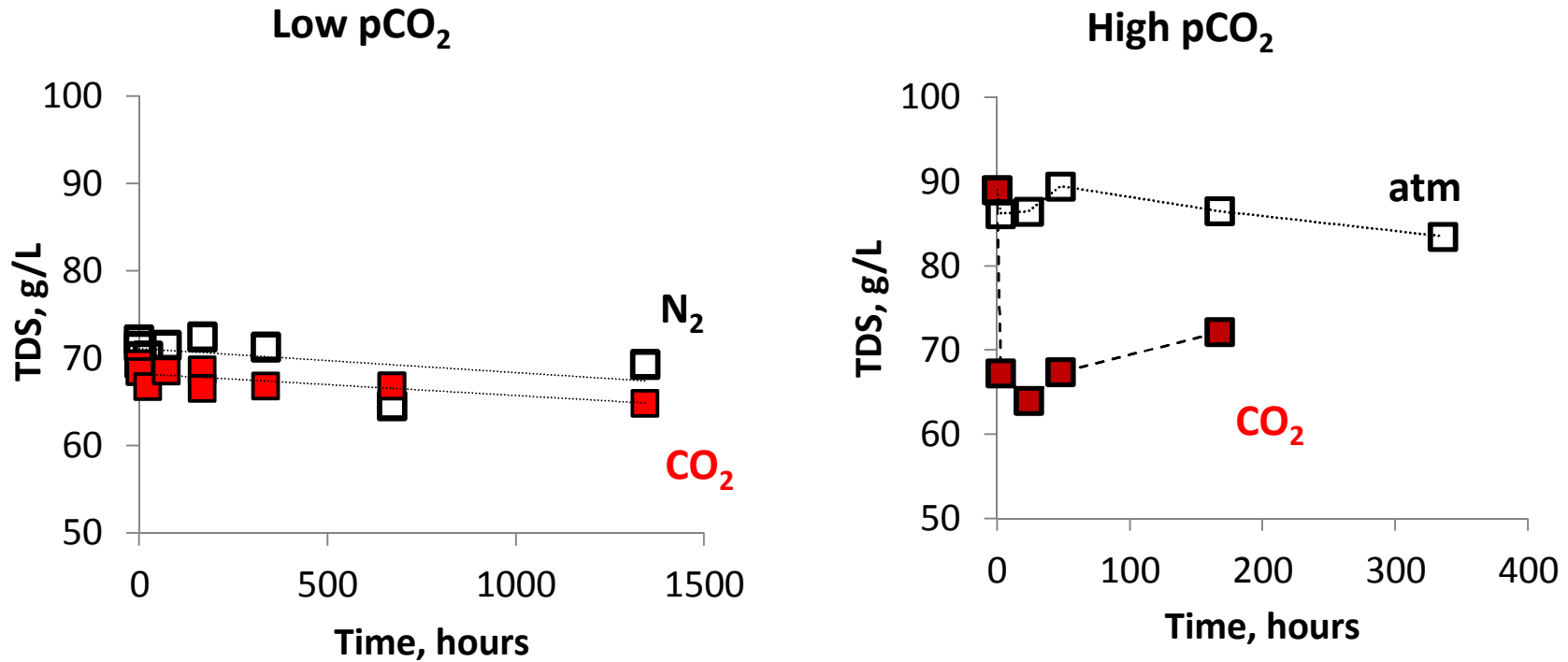
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Aqueous chemistry: Mancos



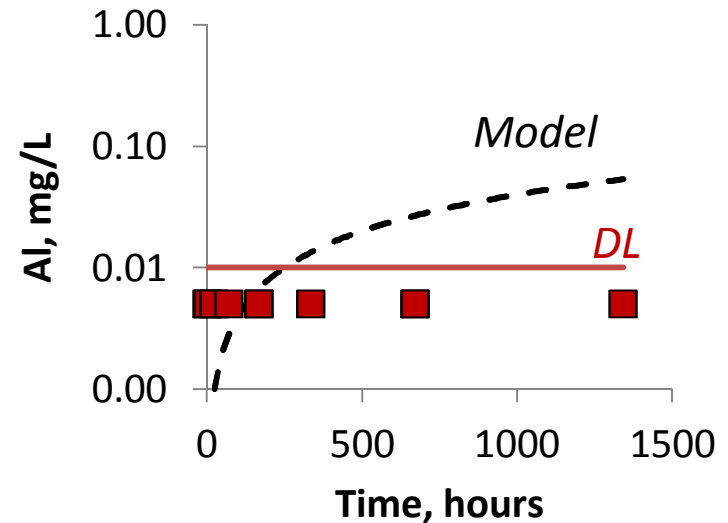
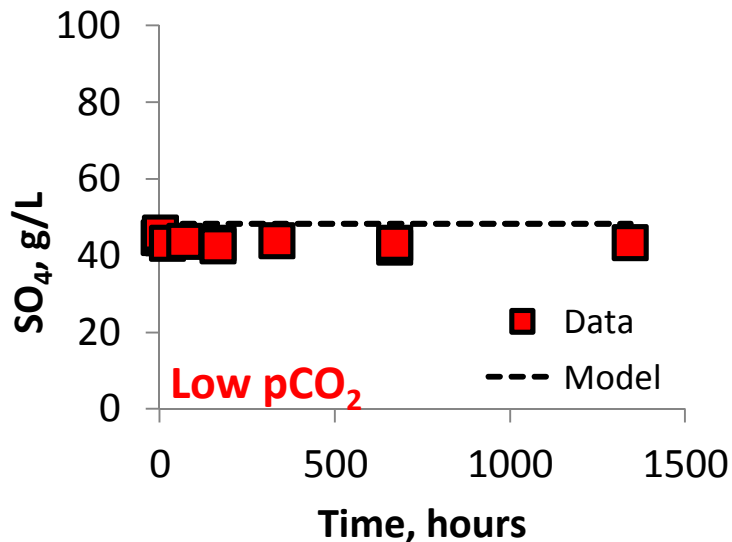
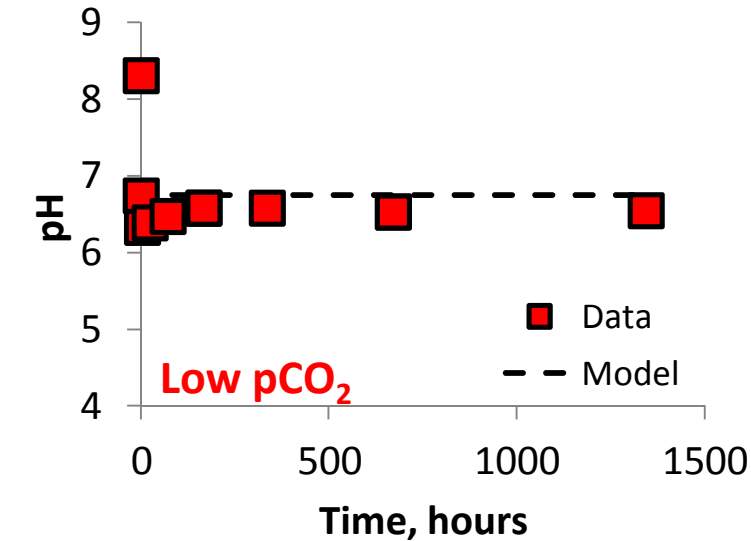
- pH is buffered by the dissolution of CO₂ into brine, and dissolution of carbonates.

Aqueous chemistry: Mancos



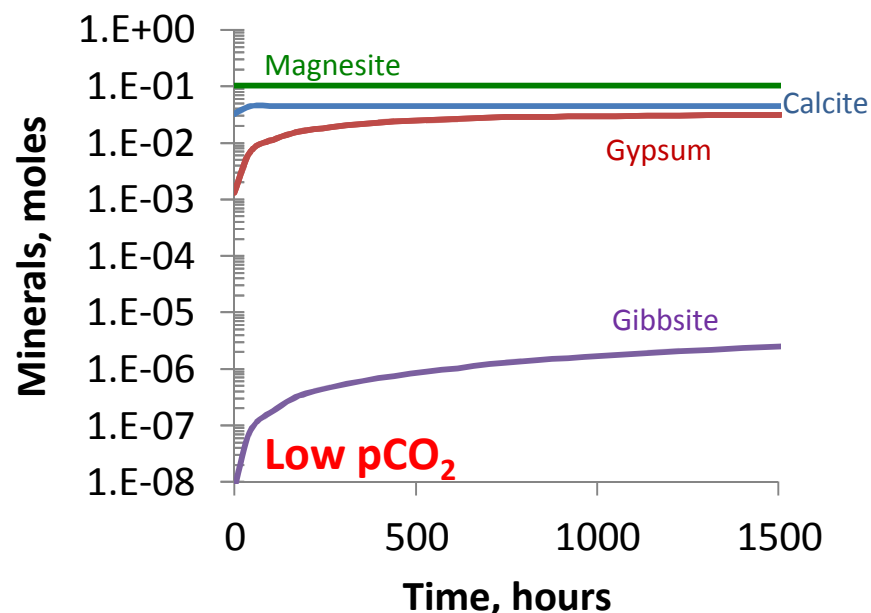
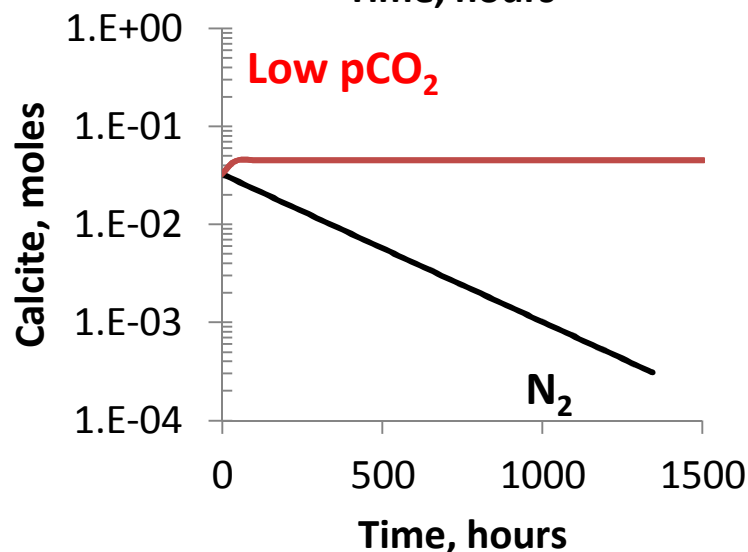
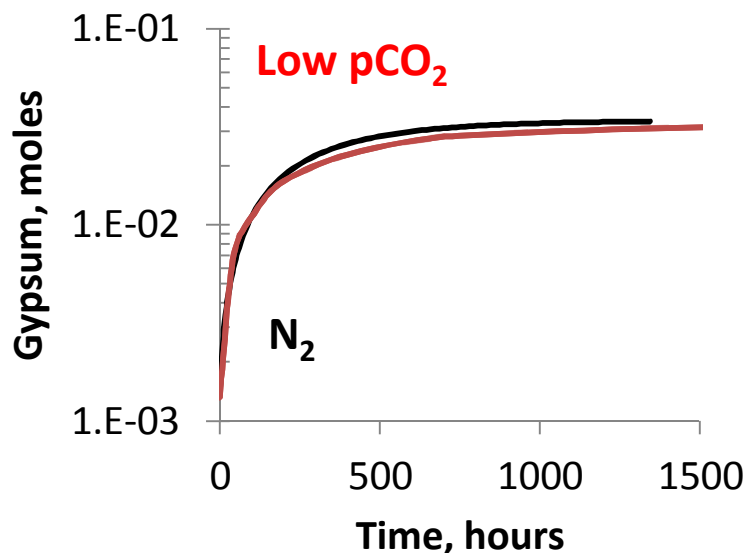
- Decrease in TDS in low and high pCO₂ reactors, and control reactors.
- Positive Na-K correlation indicates no cation exchange.
- Ca and Sr are more soluble in high pCO₂ vs. control reactors.
- Very low (microM) Fe - Fe is more soluble in high p-CO₂ -pressurized reactor.
- Al – below the detection limit.

Geochemical modeling: Mancos



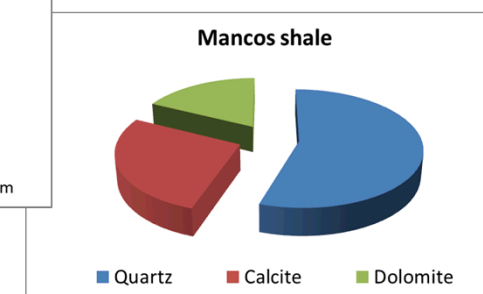
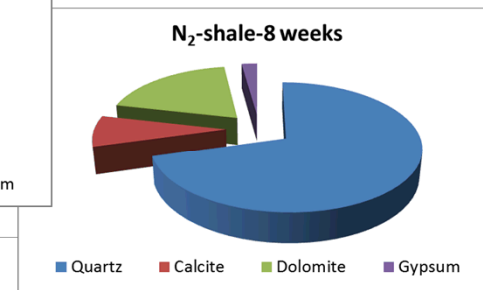
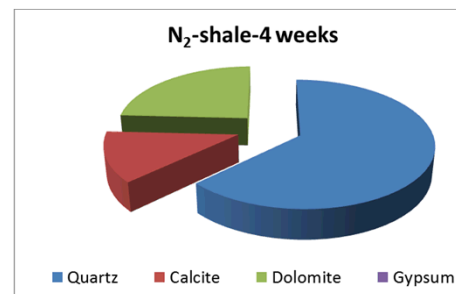
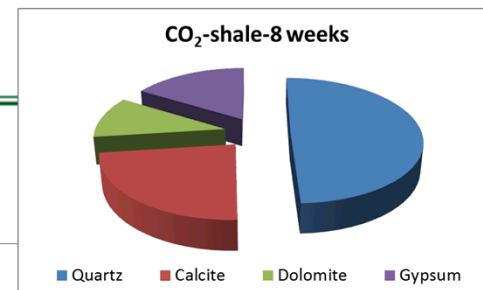
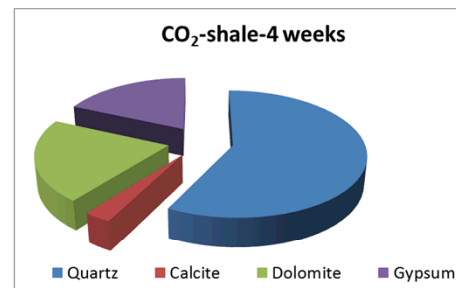
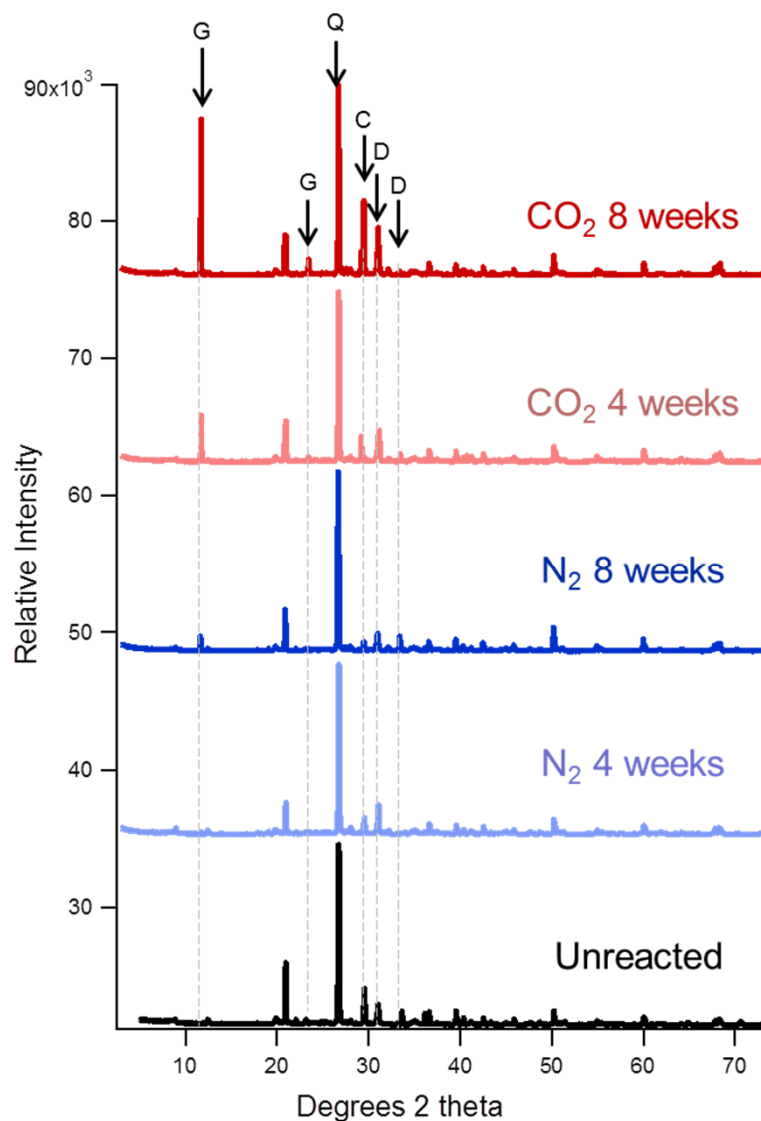
- Geochemical models capture major trends, but not everything (yet!).

Geochemical modeling: Mancos



- Calcite dissolution/precipitation and gypsum precipitation are the predominant mineralogical changes on the time scale of the experiment.
- Model predicts: minor amount of brucite in N₂-pressurized reactor, and magnesite and gibbsite— in CO₂-pressurized reactor.

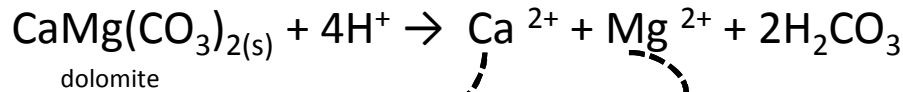
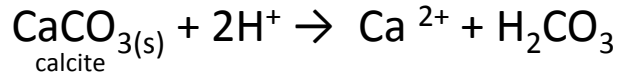
XRD, XRF: Mancos



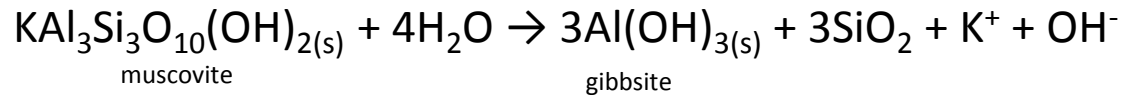
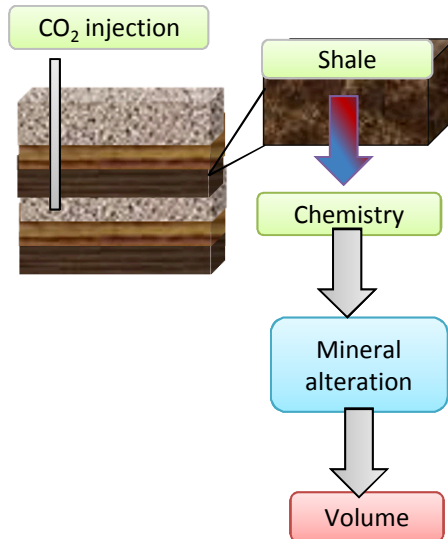
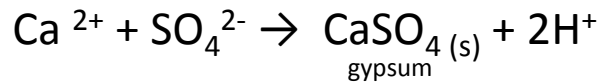
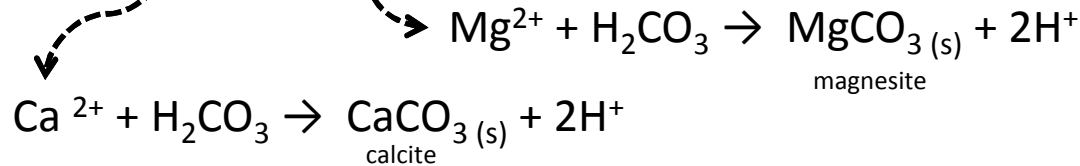
XRF

Reactor	Mg	Al	Si	S	K	Ca	Fe
CO ₂	1.78	7.66	53.16	11.32	4.23	12.55	7.61
N ₂	2.62	7.06	54.7	4.56	2.61	14.41	11.61

Mancos shale: Conclusions



Laboratory study

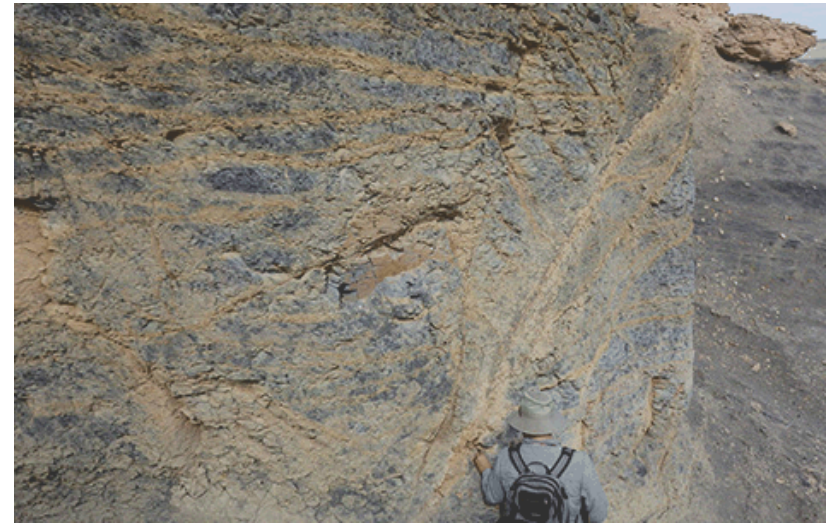
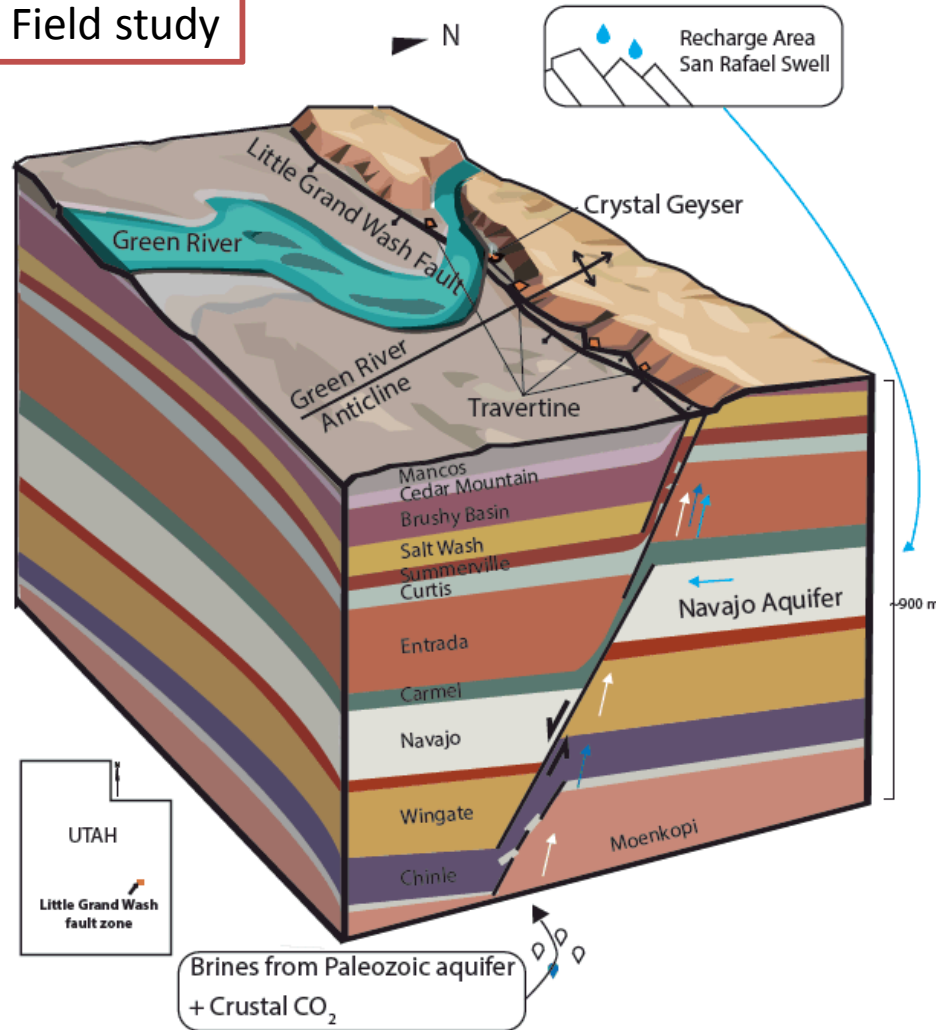


Mineral	Calcite	Albite	Dolomite	Muscovite
$\rho, \text{g cm}^{-3}$	2.71	2.62	2.84	2.82
Hardness	3	7	3.5 - 4	2 - 2.5
Mineral	Calcite	Gypsum	Magnesite	Gibbsite
$\rho, \text{g cm}^{-3}$	2.71	2.3	3	2.42
Hardness	3	2	4	3

Alteration by CO₂-brine mixture maybe causing net decrease in density and hardness.

Fractures in CO₂ caprocks: Crystal Geyser analog site

Field study



Active on 10^2 - 10^5 year time scales



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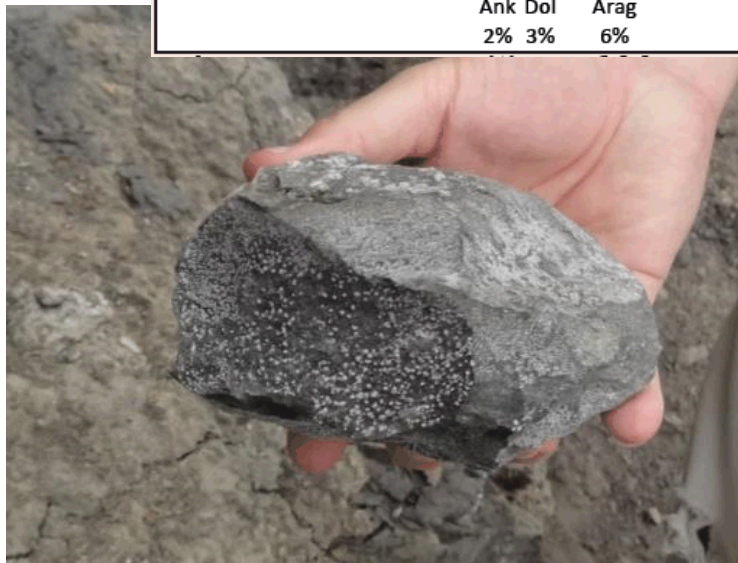
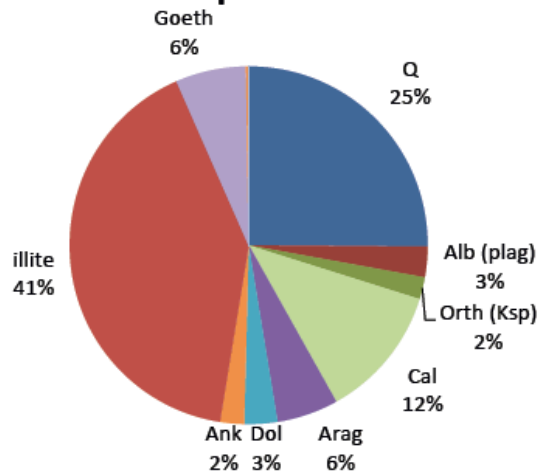
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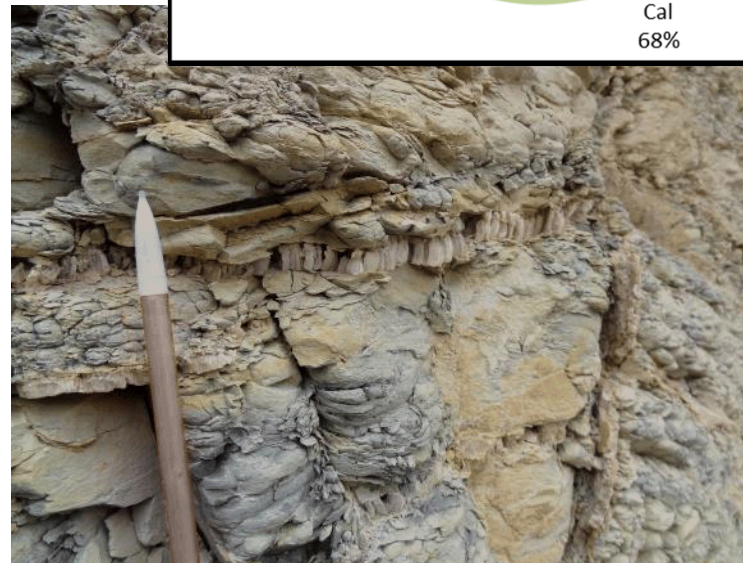
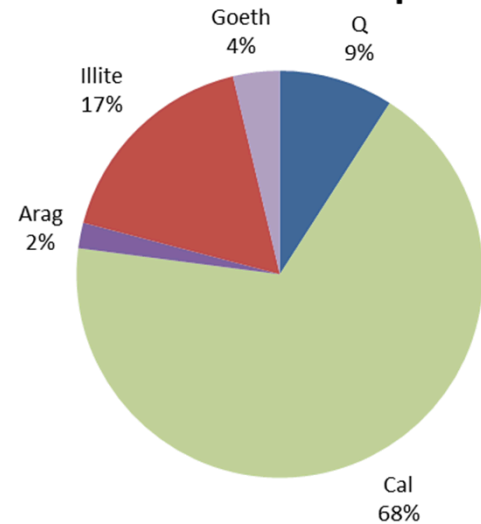
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Compositional changes of mudrock

**Unaltered Mancos Avg.
Composition**



Altered Mancos Composition



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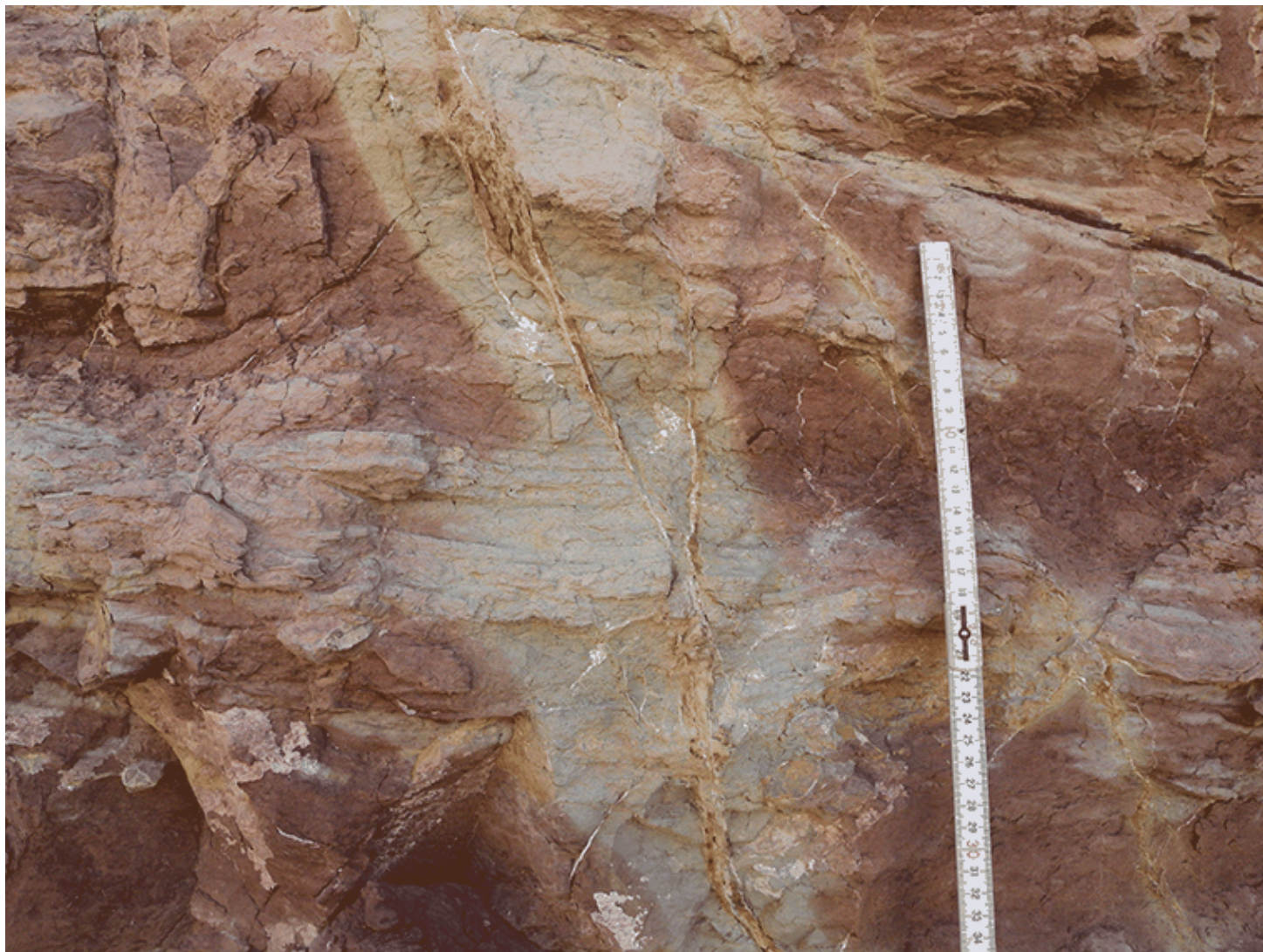
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Field fracture characterization in natural CO₂ systems



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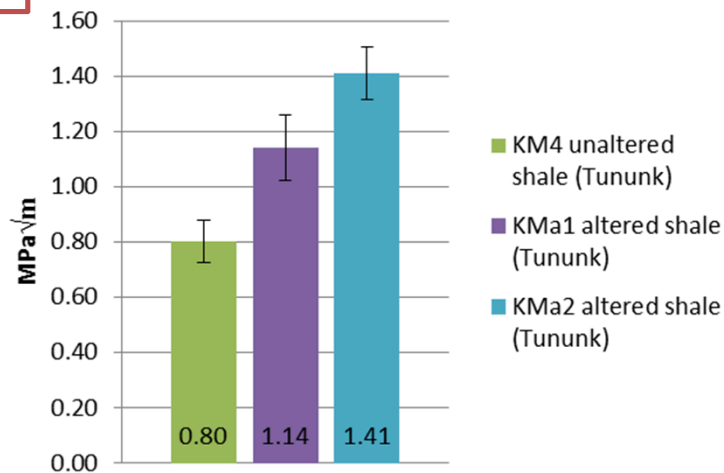


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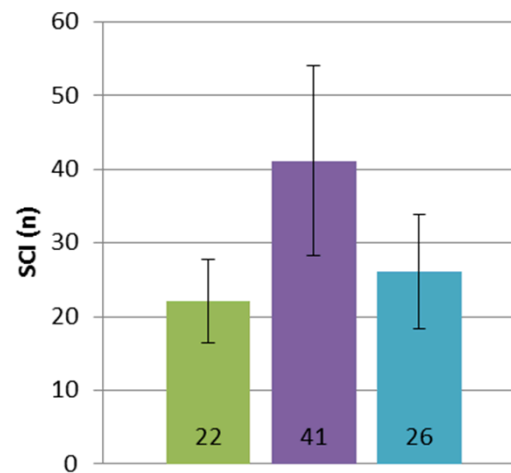
Double torsion testing: Fracture toughness, subcritical crack index n (SCI)

Field study

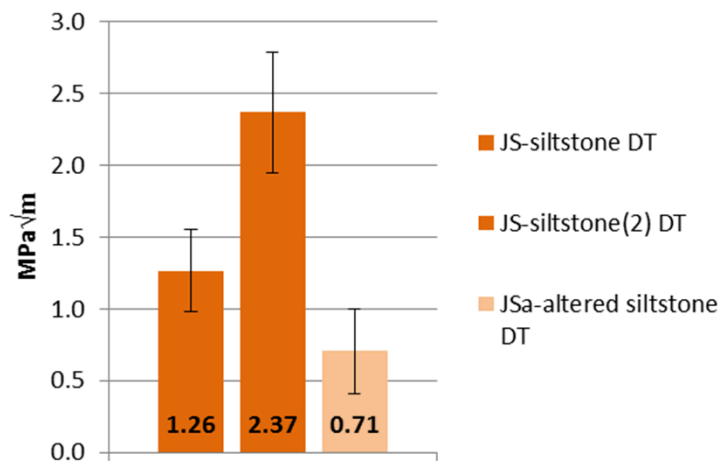
Mancos K_{IC}



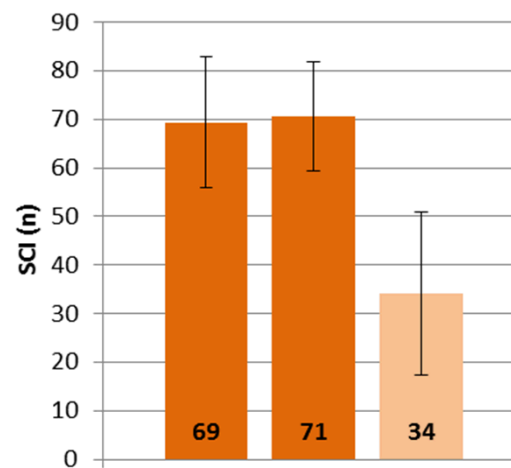
Mancos SCI



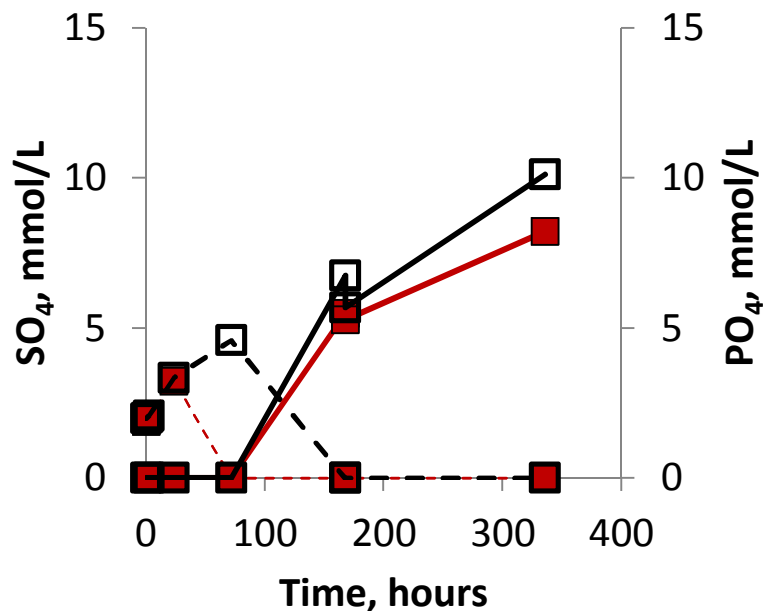
Summerville K_{IC}



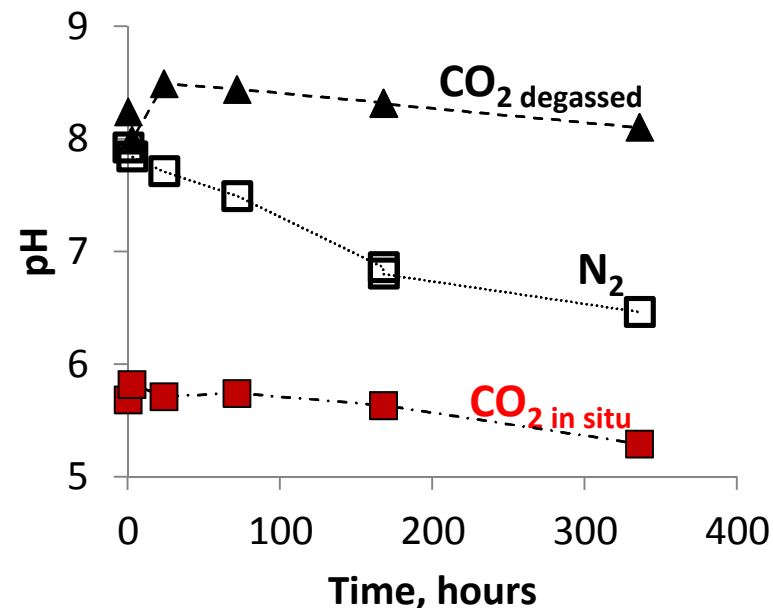
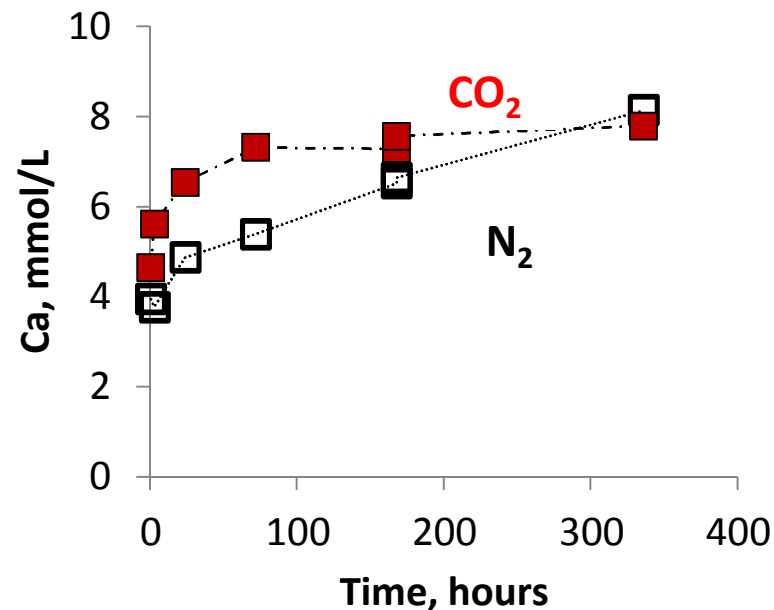
Summerville SCI



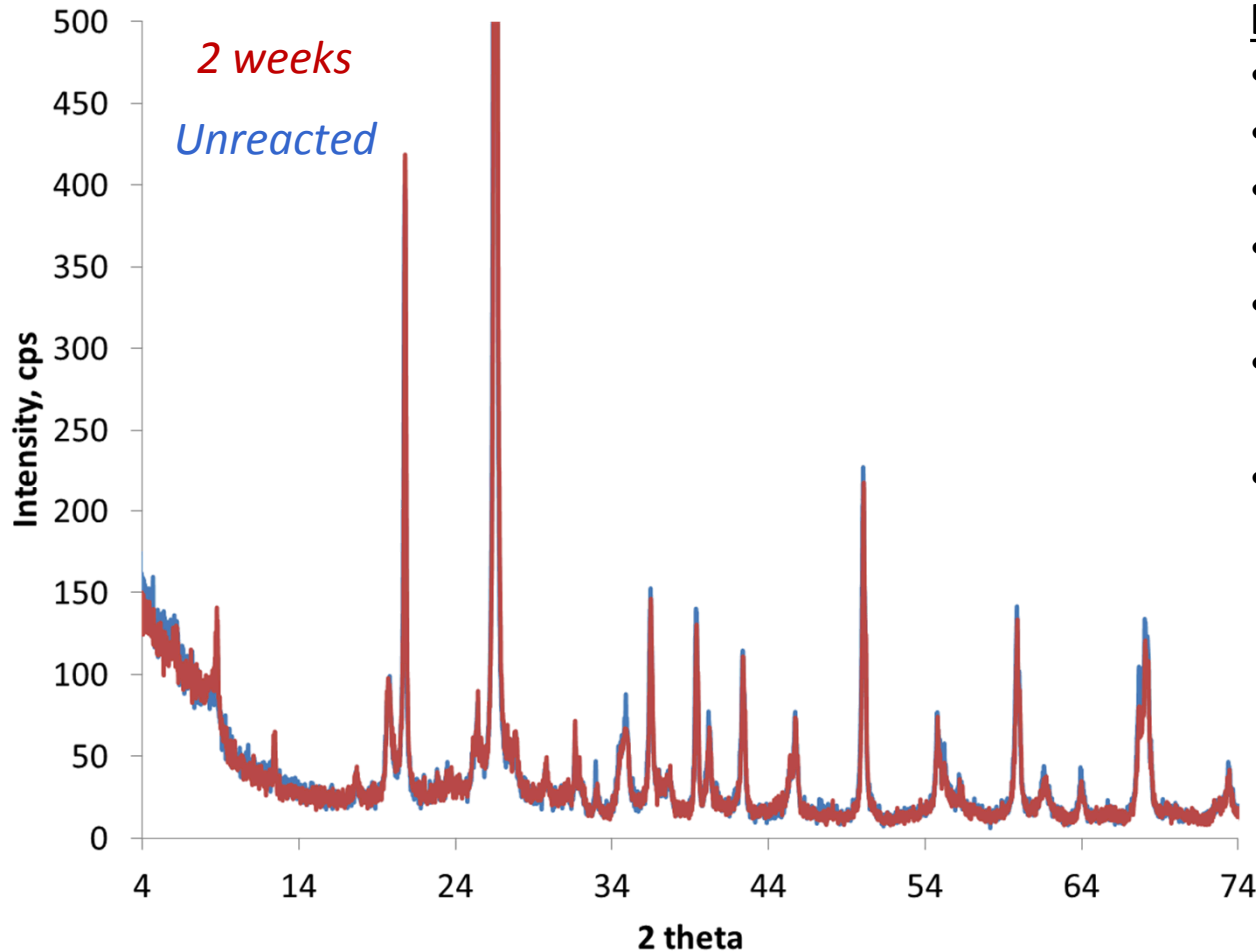
Aqueous chemistry: Woodford



- TDS is ~ constant
- Ca, Mg, and Si are more soluble in CO_2 vs. N_2 reactor.
- Al and Fe - very low, $\mu\text{mol/L}$ level (Al), 0.1 $\mu\text{mol/L}$ (Fe).
- No Na-K cation exchange
- SO_4 consumption, PO_4 mobilization.



XRD: Woodford



Initial composition:

- Quartz
- Illite, mica
- Chlorite
- Anhydrite
- Calcite (small amount)
- Plagioclase
- No dolomite

What's dissolving:

- Quartz
- Calcite

After 2 weeks



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Future work

Experiments

Geochemistry	Geomechanics
Alteration of Woodford and Eau Claire shales in brine-CO ₂ systems at high and low pressure of CO ₂	Micromechanical experiments: nano-pillar indentation to measure mechanical changes due to alteration by CO ₂ .
Effect of gas impurities (O ₂ , and potentially NO _x , and SO _x) on the minerals alteration in CO ₂ -brine systems.	Micromechanical experiments: indentation and scratch test to measure mechanical alteration by CO ₂ .

Modeling

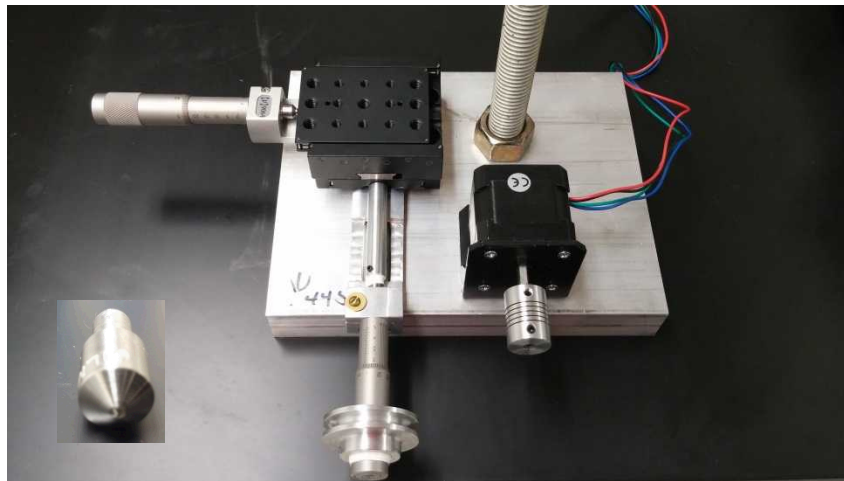
Geochemistry	Geomechanics
Geochemical modeling to interpret observed geochemical changes and construct predictive models for the carbon storage time scales (1000 years and longer).	Integrating computation with micromechanical (indentation and scratch) experiments, using the DEM and FEM approaches with coupling of geochemistry and mechanics.



Micro-mechanical characterization: scratch tests

- Micromechanical experiments (scratch test) to measure mechanical alteration by CO₂ and identify characteristic time-scales and length-scales involved in the geochemical reactive transport processes.

Apparatus for scratch test

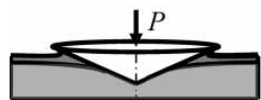


Micromechanical Properties

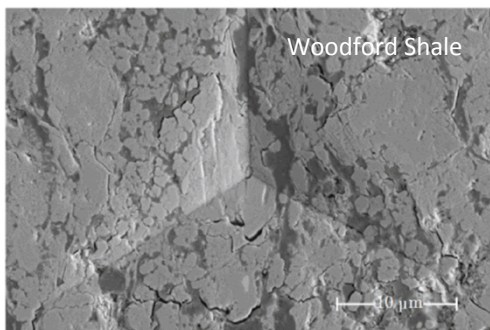
Micron scale laboratory experiments on unaltered and chemically altered shales to assess changes in mechanical properties like hardness, Young's Modulus, and unconfined compressive strength due to chemical reactions likely to occur with scCO_2 in GCS. Results can be applied to assess long-term caprock stability.

Nano-pillar indentation

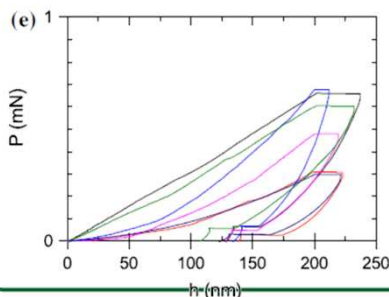
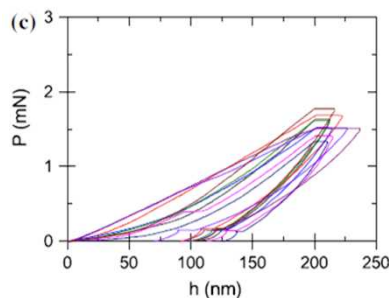
An AFM based tool, this utilizes a rigid punch to indent a machined smooth surface of a sample to calculate hardness and Young's modulus. Automation allows for high density surface coverage to map changes in properties. Different indentation depths test different volumes of materials.



Tang & Ngan, 2007

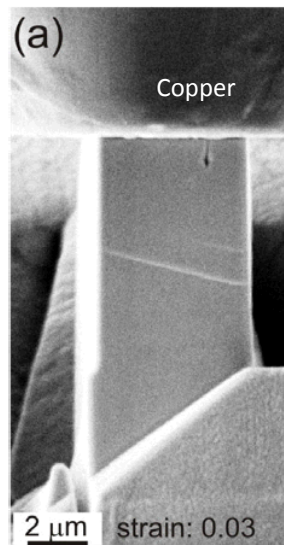


Bennett et al., 2015

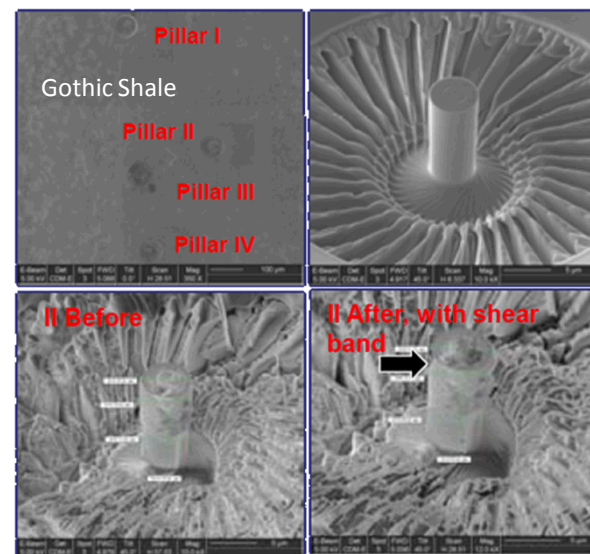


Micropillar compression

Analogous to standard geomechanics tests, pillars are machined into sample surface using FIB, and deformed with a rigid punch in SEM to measure UCS and Young's modulus. The small size of the pillars allows the testing of individual mineral constituents to determine mechanical properties.



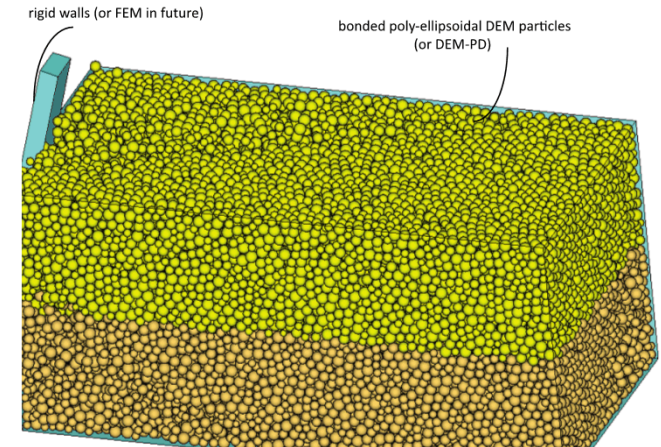
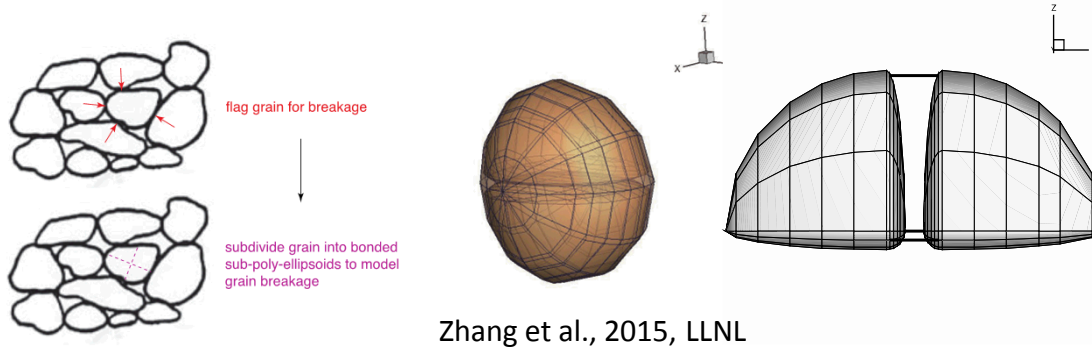
Kiener et al., 2011



Dewers et al., 2010

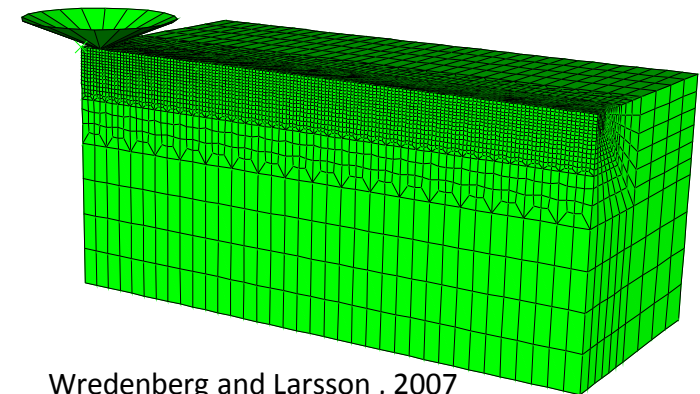
Computational model

- **Discrete Element Method (DEM) Particle Fracture Model**
 - Poly-ellipsoidal DEM Particle Fracture Model (bonding for chemistry effect)



Rizo, 2013, University of Pittsburgh, PhD Thesis

- **Finite Element Method (FEM)**
 - XFEM-Presto (Sierra Mechanics)
 - Kayenta as constitutive model



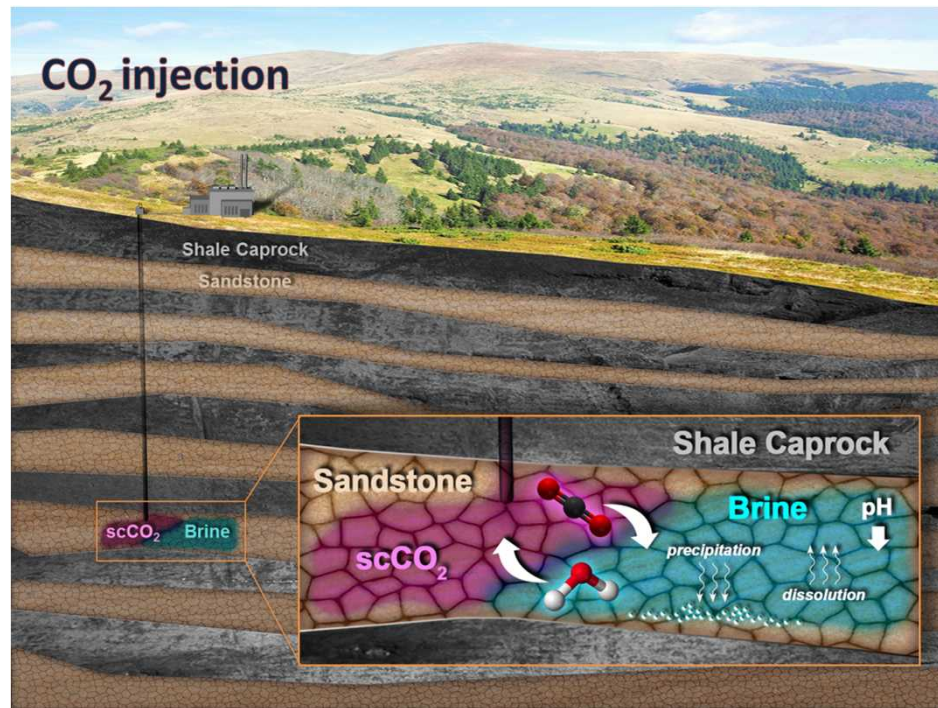
CFSES Research Challenges and Efforts

Sustaining Injectivity

Storage Efficiency

Controlling Emergence

Long-term security of CO₂ storage



Caprock alteration experiments will help understanding the coupled geochemical-geomechanical processes and developing strategies for controlling CO₂ leakage pathway development.

Alteration by brine-CO₂ influences mechanical integrity of rock types in different ways depending on mineral make up and brine chemistry, and extent of alteration.



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Extra slides



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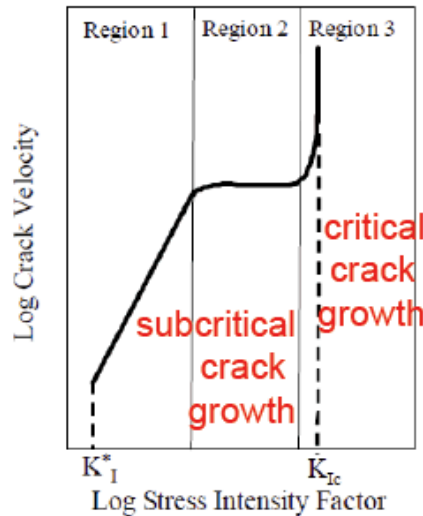
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Subcritical fracture growth



K_I^* = stress corrosion limit
 K_{IC} = fracture toughness

After Atkinson, 1984

$$V = A \left(\frac{K_I}{K_{IC}} \right)^n$$

V: fracture propagation velocity

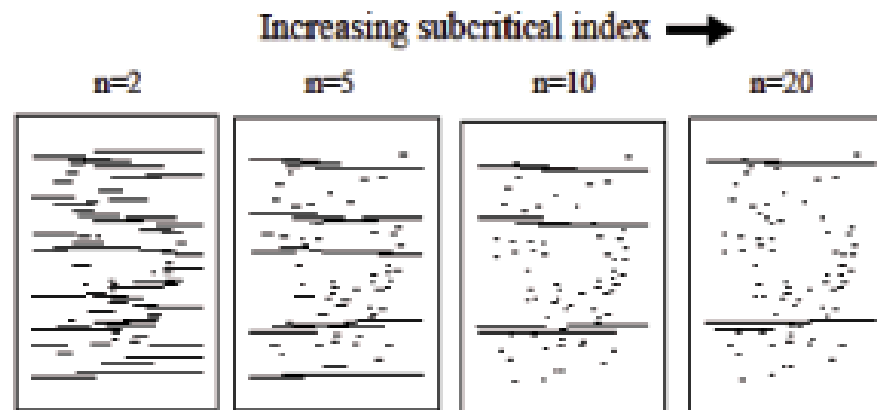
K_I : mode-I stress intensity factor,

K_{IC} : mode-I critical stress intensity factor (or fracture toughness)

A: a pre-exponential constant (Atkinson, 1984; Swanson 1984)

n: velocity exponent (SCI)

Results of
 subcritical crack
 growth affecting
 fracture network
 geometry



Increasing spacing
 Decreasing variance

Holder et. al, 2001



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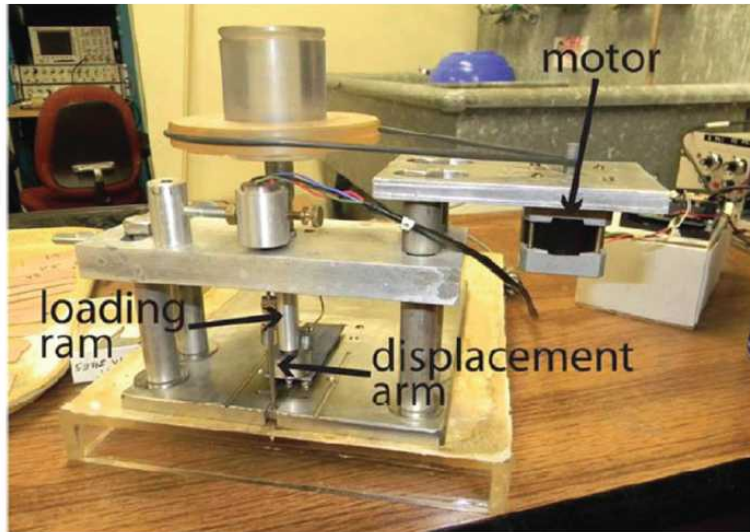
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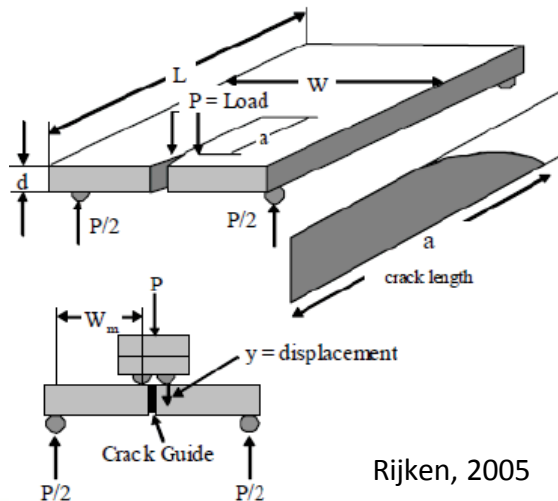
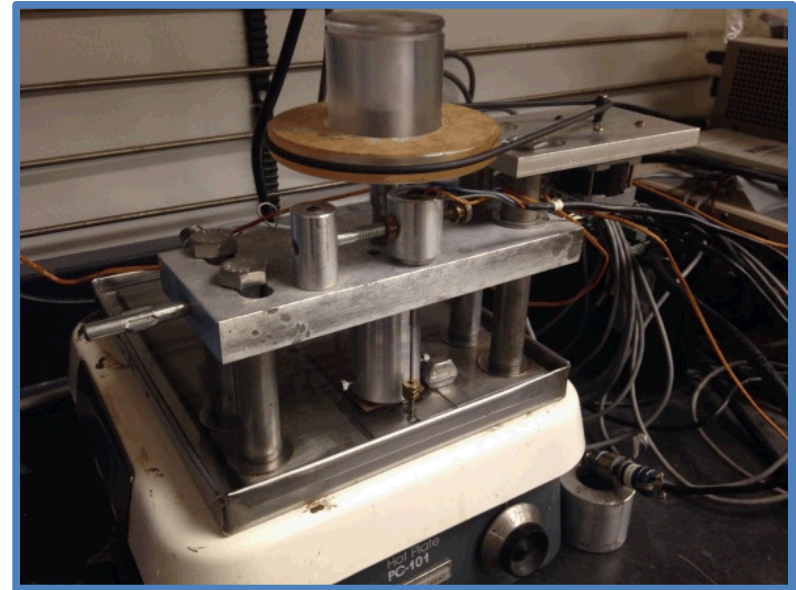
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Double torsion fracture mechanics testing

DOUBLE TORSION (DT)



Hot plate &
tray for
temperature
and fluid
control



Rijken, 2005



Sample geometry



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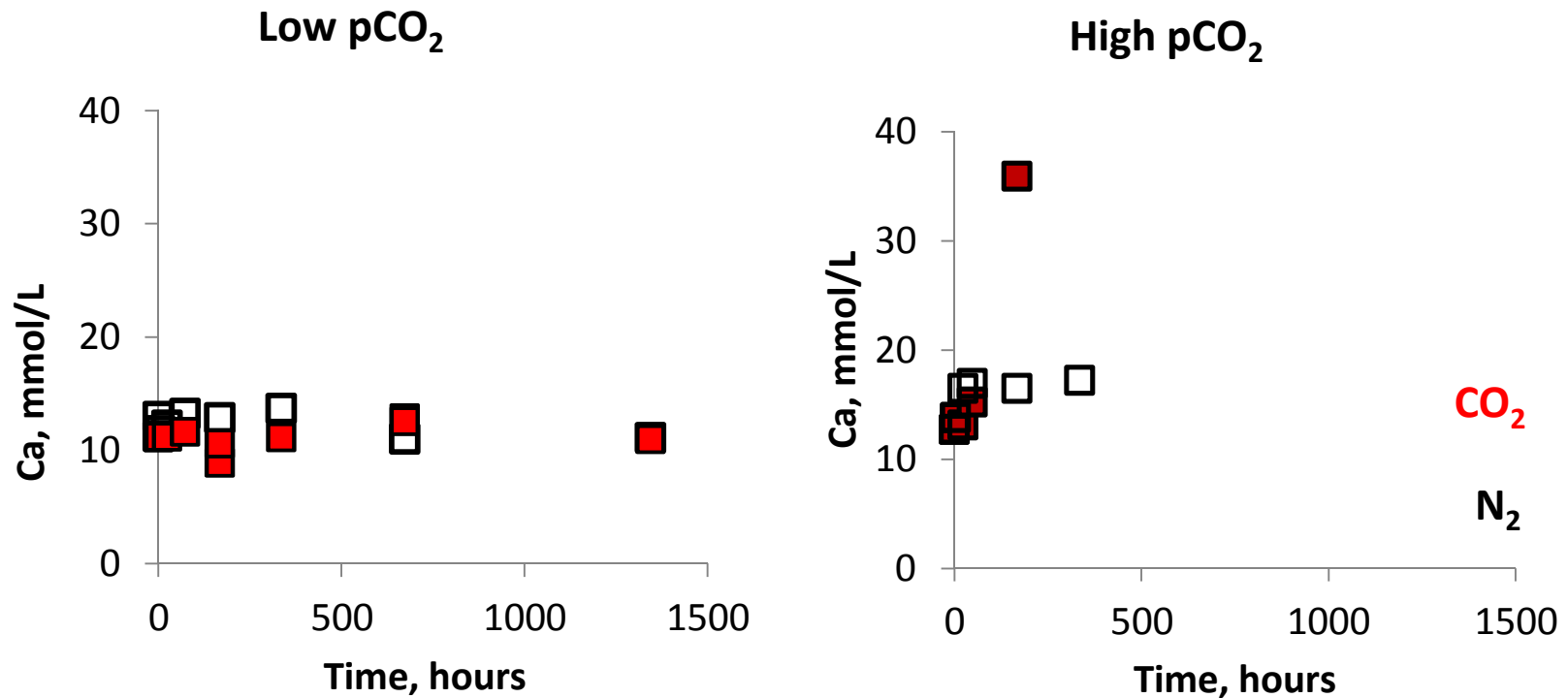
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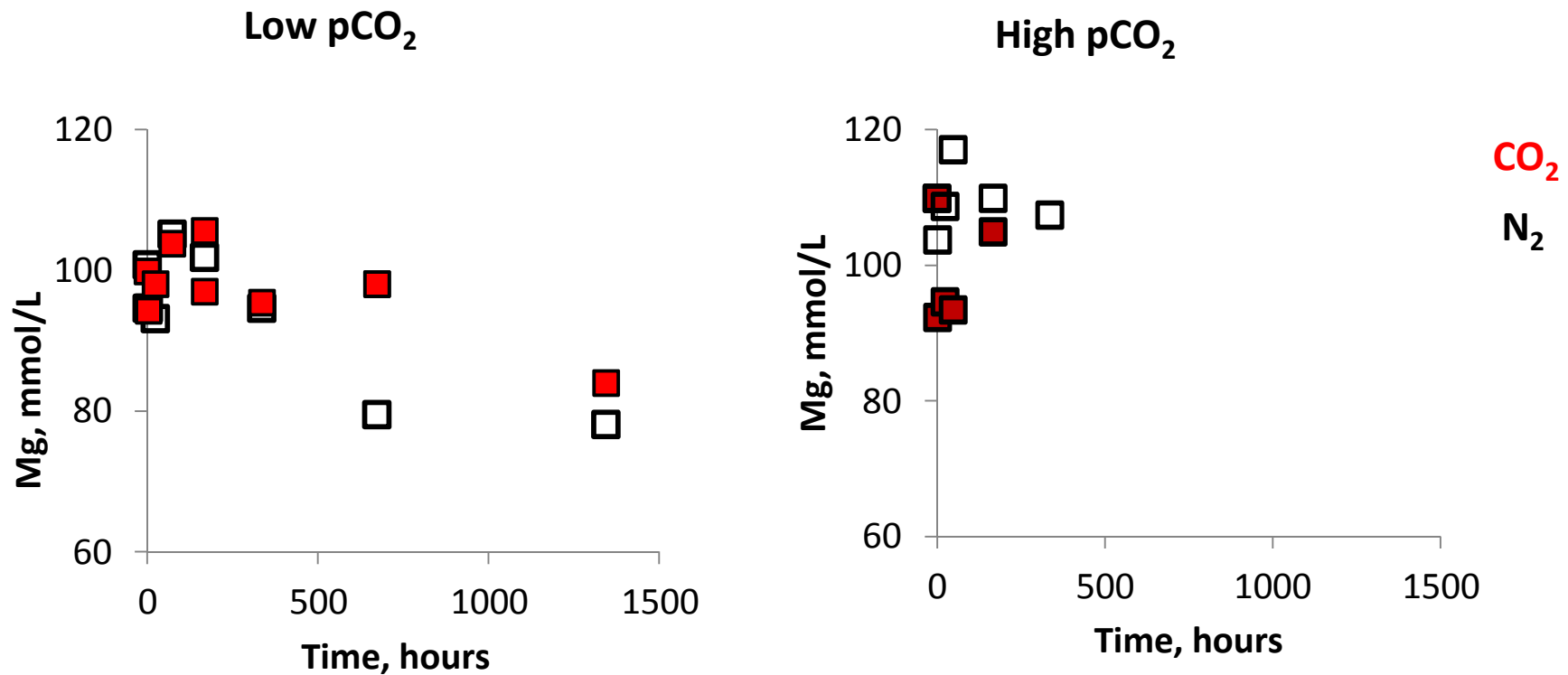
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Aqueous chemistry: Mancos



- Ca is more soluble in high p-CO₂-pressurized reactor

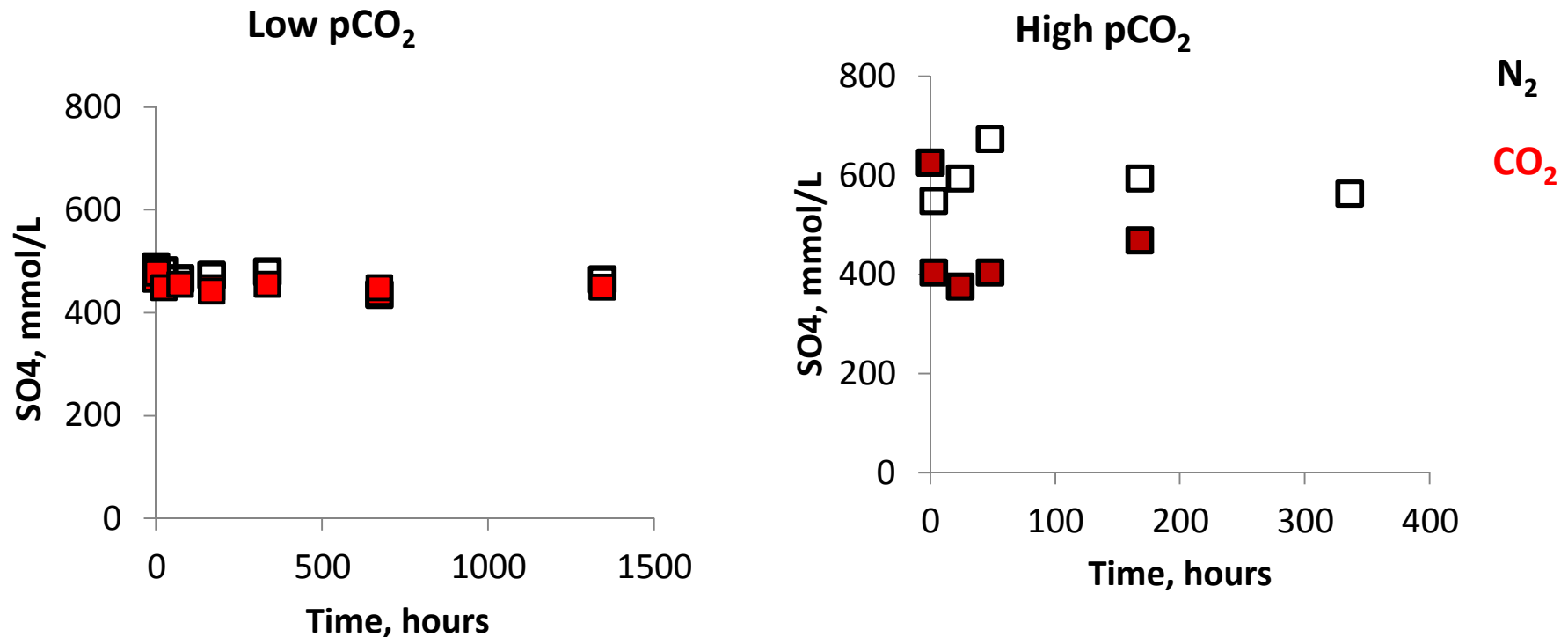
Aqueous chemistry: Mancos



- Ca, Mg, Si, Sr, and Fe are more soluble in CO₂ vs. N₂ and atm reactors; Al – not detected.

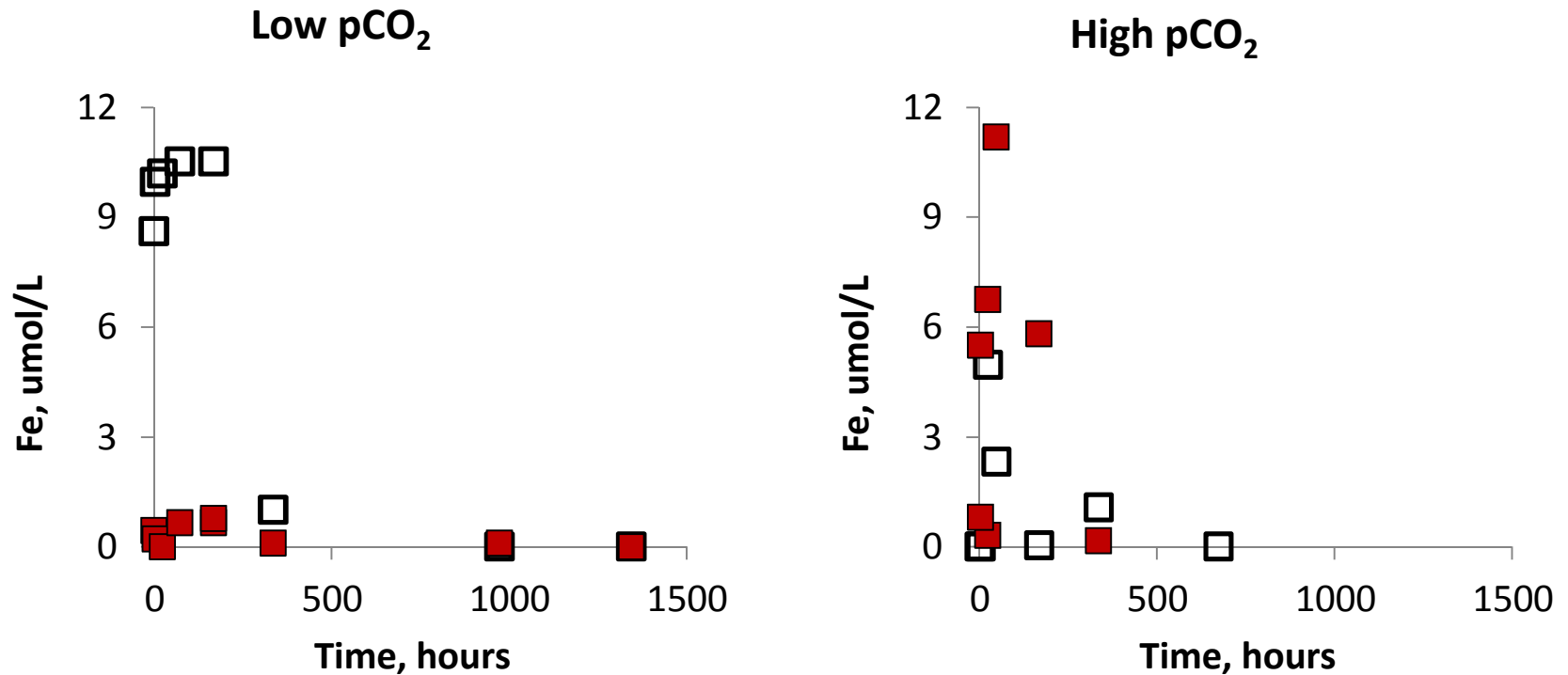


Aqueous chemistry: Mancos



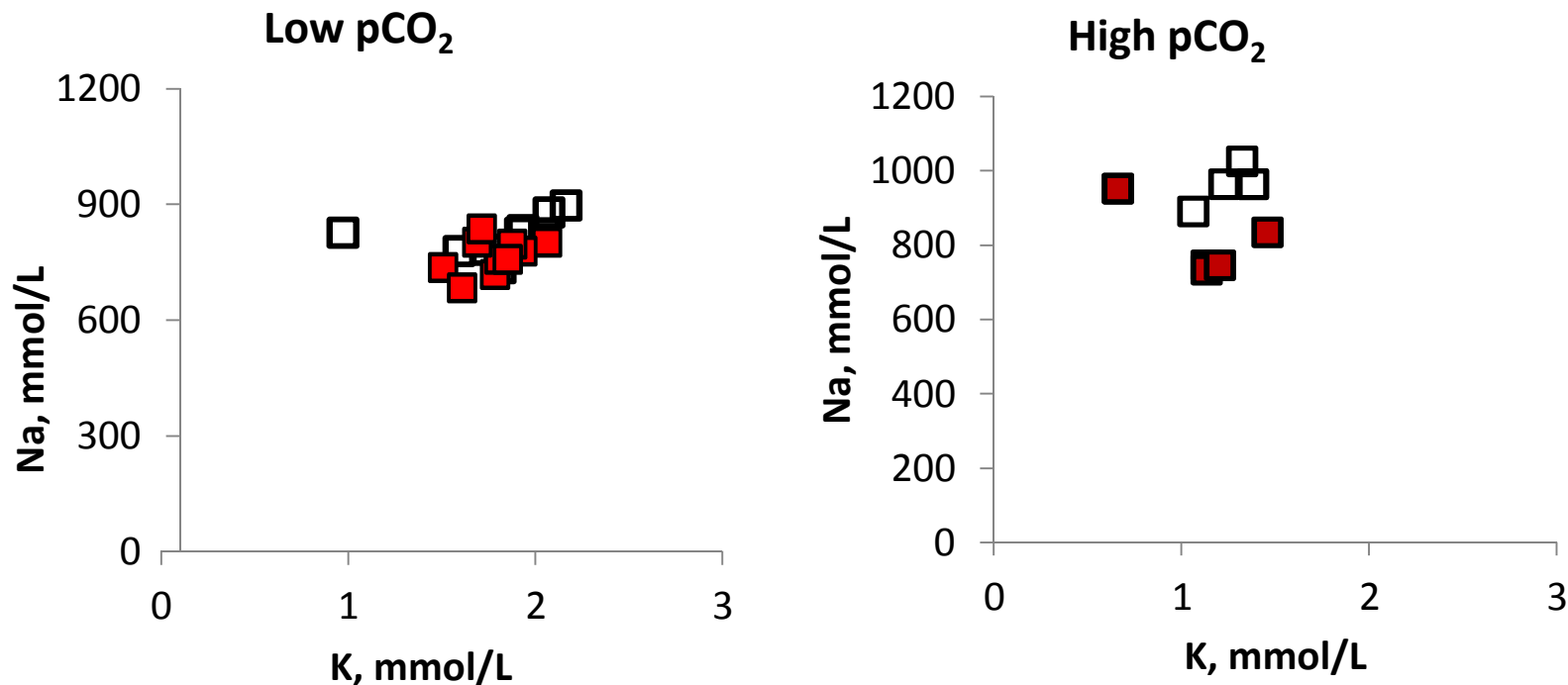
- Ca, Mg, Si, Sr, and Fe are more soluble in CO_2 vs. N_2 -pressurized reactor; Al – not detected.
- Positive Na-K correlation indicates no cation exchange.

Aqueous chemistry: Mancos



- Fe is more soluble in high p-CO₂ -pressurized reactor

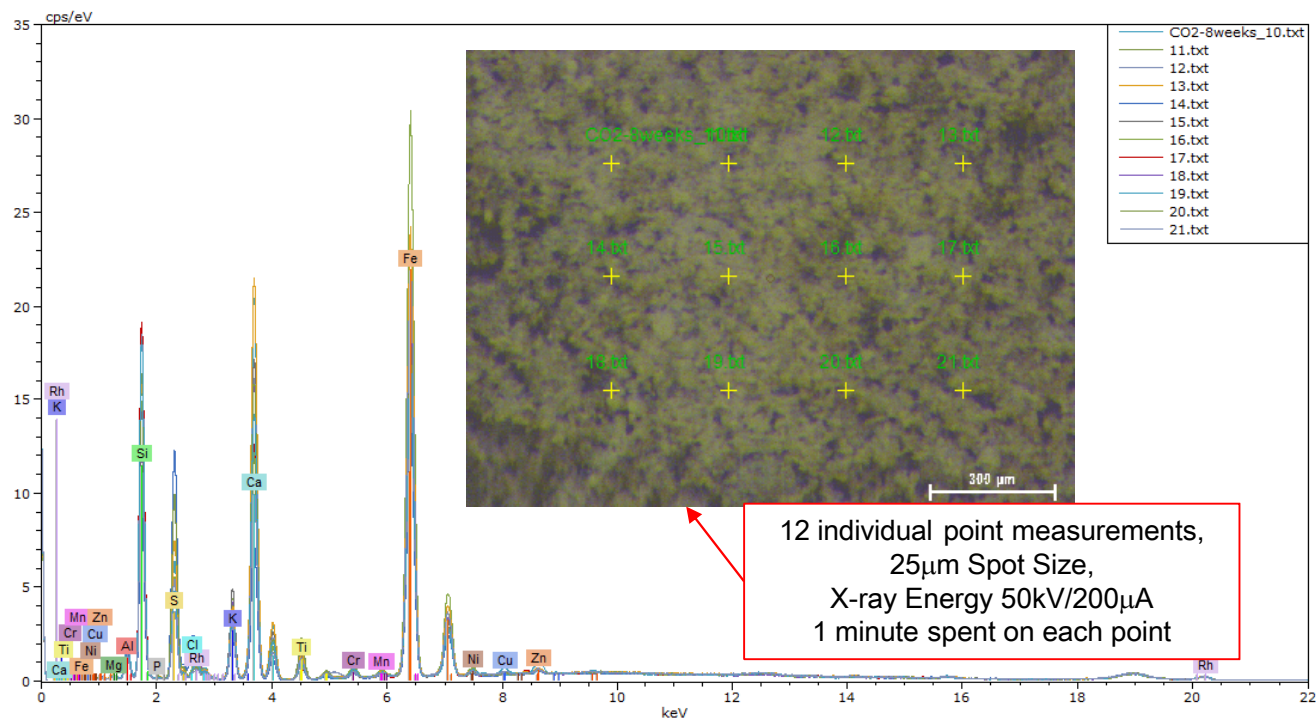
Aqueous chemistry: Mancos



- Positive Na-K correlation indicates no cation exchange.



XRF: Mancos



Reactor	Mg	Al	Si	S	K	Ca	Fe
CO ₂	1.78	7.66	53.16	11.32	4.23	12.55	7.61
N ₂	2.62	7.06	54.7	4.56	2.61	14.41	11.61

Geochemical Modeling: Mancos

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

Initial brine

pH	7.44	
Cl ⁻	1589	mg/L
NO ₃ ⁻	4.1	mg/L
SO ₄ ²⁻	47251	mg/L
K ⁺	20.5	mg/L
Ca ²⁺	484	mg/L
Na ⁺	19000	mg/L
Mg ²⁺	2700	mg/L
Fe ²⁺	2	mg/L

Mineral

wt.%

k, mol cm⁻² sec⁻¹

Quartz	80.5	1×10 ⁻¹⁷
Albite	8.3	1×10 ⁻¹⁶
Dolomite	7.6	1×10 ⁻¹²
Calcite	4.9	1×10 ⁻⁸
Muscovite	2	1×10 ⁻¹⁴
Kaolinite	1	1×10 ⁻¹⁴
Pyrite	1	2.5×10 ⁻¹⁵
Hematite	1	2.5×10 ⁻¹⁴

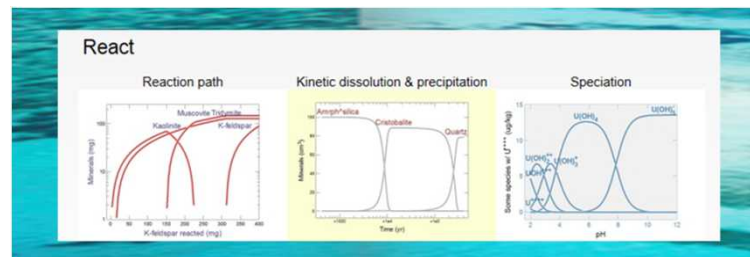


Image source: <http://www.gwb.com/>

