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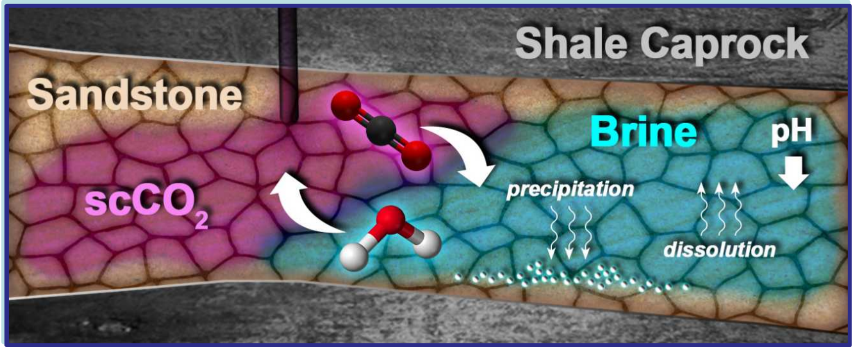

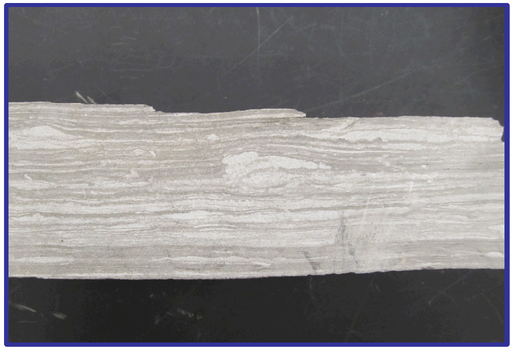

Mancos shale-brine-CO_2 interactions and the long-term stability of shale caprock

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U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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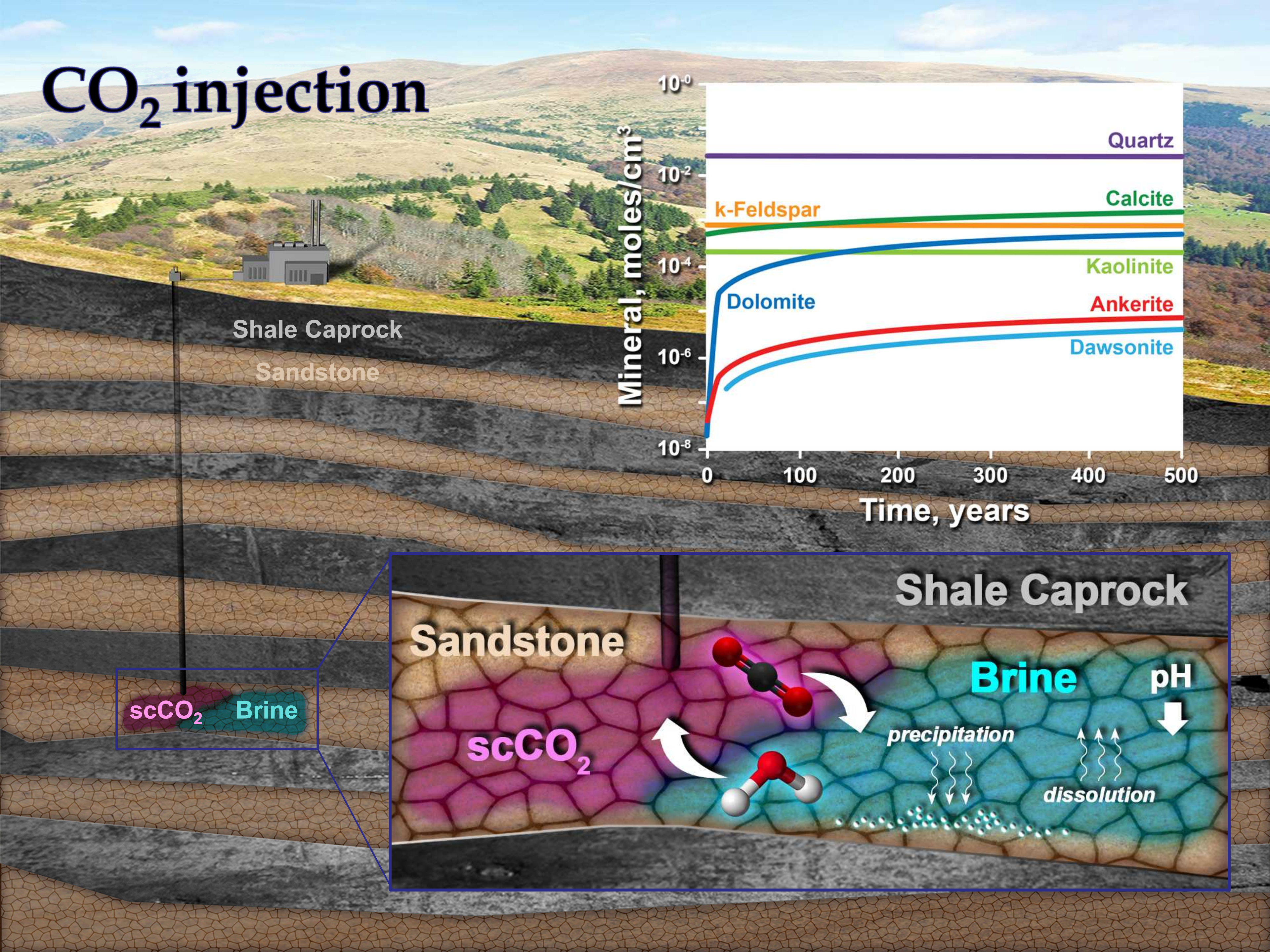
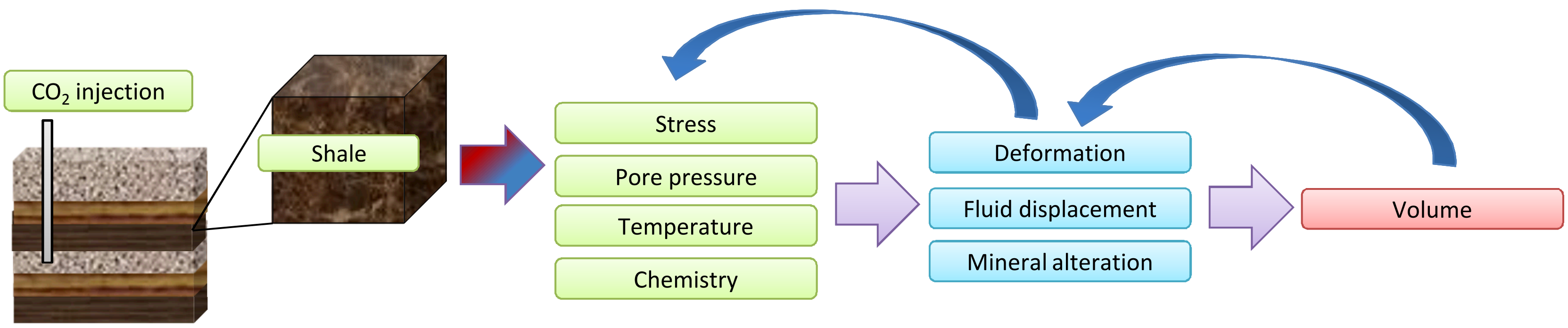


CO$_2$ injection
Shale Caprock
Sandstone
scCO$_2$
Brine
Mineral, moles/cm^3
10^{-0}
10^{-2}
10^{-4}
10^{-6}
10^{-8}
Quartz
Calcite
k-Feldspar
Kaolinite
Dolomite
Ankerite
Dawsonite
0
100
200
300
400
500
Time, years
Shale Caprock
Sandstone
Brine
pH
scCO$_2$
precipitation
dissolution

Geochemical response triggered by the injection of CO_2

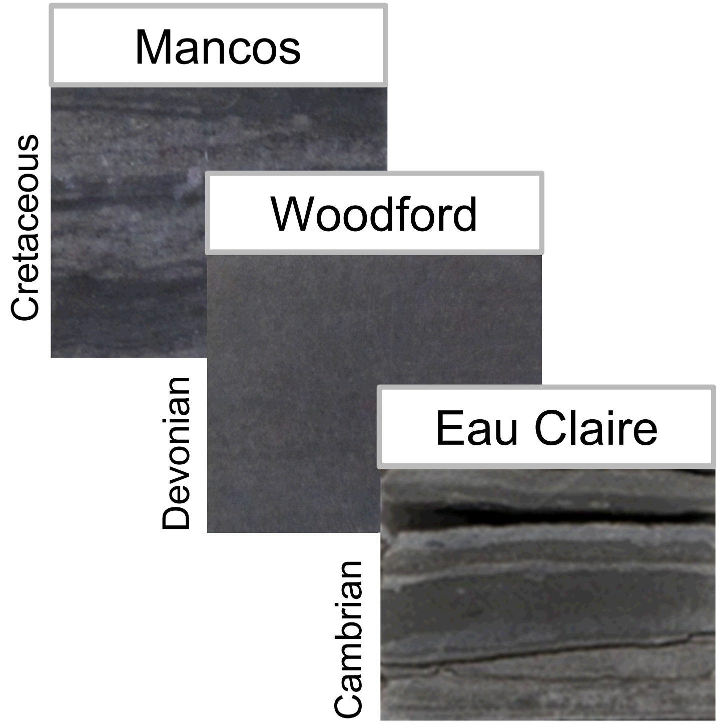
- At geologic storage PT: CO_2 is supercritical ($scCO_2$).
- $scCO_2$ stimulates **geochemical responses**: acidification of parent brine, and dehydration of mineral surfaces.[1-3, 8]
- Experimental and field studies: geochemical reactions differ significantly for different rock assemblages and brine 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 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

Project objectives

Establish quantitative relationships between chemical reactions triggered by the addition of supercritical CO_2 and changes in nano- to micro-scale mechanical properties of shale.



- 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.

Mineral alteration

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

$$\mathbf{Fe_{2.5}Mg_{2.5}Al_2Si_3O_{10}(OH)_8} + \mathbf{2.5CaCO_3} + 5CO_2 \rightarrow \quad [2]$$

chlorite, calcite

$$\rightarrow 2.5FeCO_3 + 2.5MgCa(CO_3)_2 + Al_2Si_2O_5(OH)_4 + SiO_2 + 2H_2O$$

siderite, dolomite, kaolinite, chalcedony

$$\mathbf{KMg_{2.87}Si_{3.07}Al_{1.23}O_{10}(OH)_2} + H_2CO_3 + Na^+ + Cl^- \rightarrow \quad [3]$$

phlogopite

$$\rightarrow (K,H_3O)(Al,Mg)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)] + SiO_{2(am)} + AlOOH_{(s)} +$$

illite, diaspore

$$+ NaCl + K^+ + Mg^{2+} + Al^{3+} + H_4SiO_4 + HCO_3$$

$$\mathbf{2NaAlSi_3O_{8(s)}} + H^+ + 0.5H_2O \rightarrow AlO(OH)_{(s)} + 0.5Al_2Si_2O_5(OH)_{4(s)} + 2Na^+ + 5SiO_2 \quad [4]$$

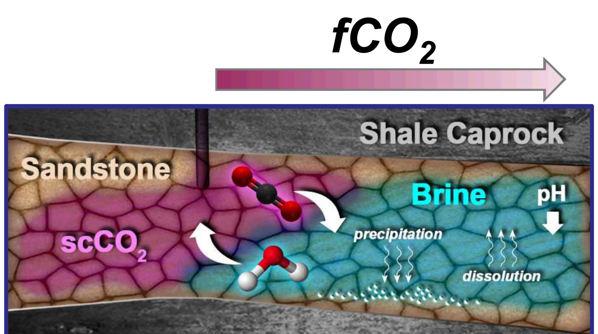
albite, boehmite, kaolinite

$$\mathbf{CaCO_{3(s)}} + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$$

calcite

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

Shale alteration in brine-CO_2 mixtures



- Stirred reactors pressurized with **CO_2**
- Control reactors – pressurized with $\mathbf{N_2}$ or buffered by ambient atm
- Powdered shale (A_{BET} = 8.3 m^2 g^{-1}) + **brine**
- Sample brine and solids at time intervals
- Analysis by IC, ICP-MS, and XRD
- Geochemical modeling

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}

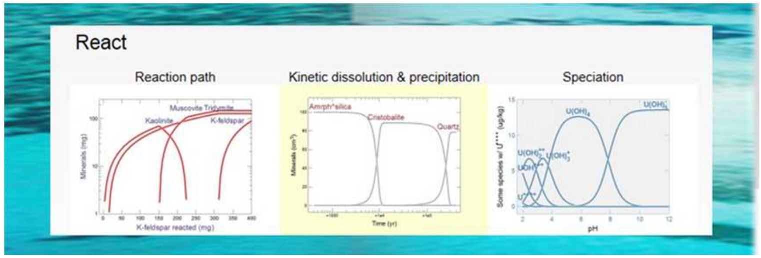


Image source: http://www.gwb.com/

Mancos shale alteration in brine-CO_2 mixtures

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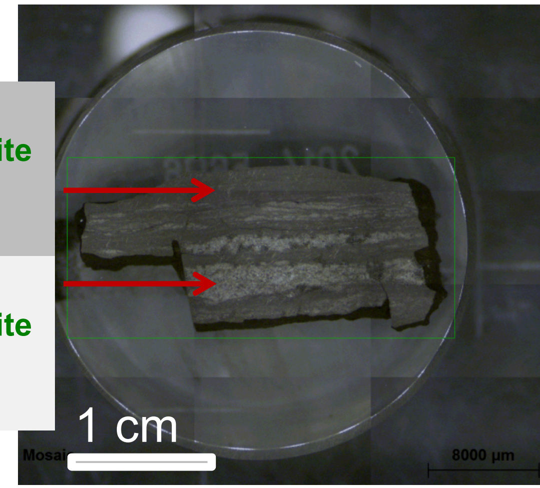
Synthetic brine*

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

Mancos Shale

Quartz, Calcite, Dolomite, Muscovite Albite
Pyrite, Hematite

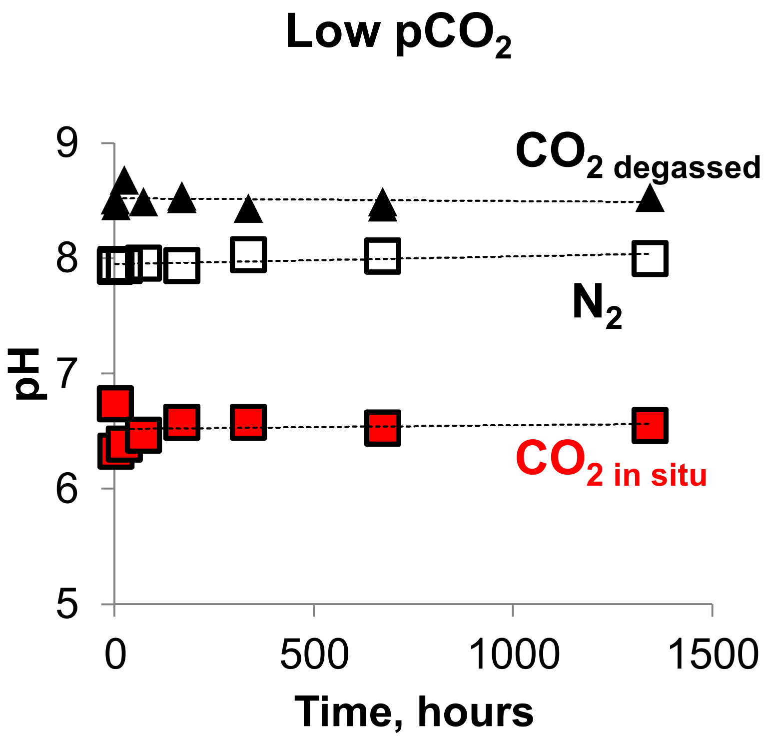
Quartz, Calcite, Dolomite, Muscovite Albite
Kaolinite

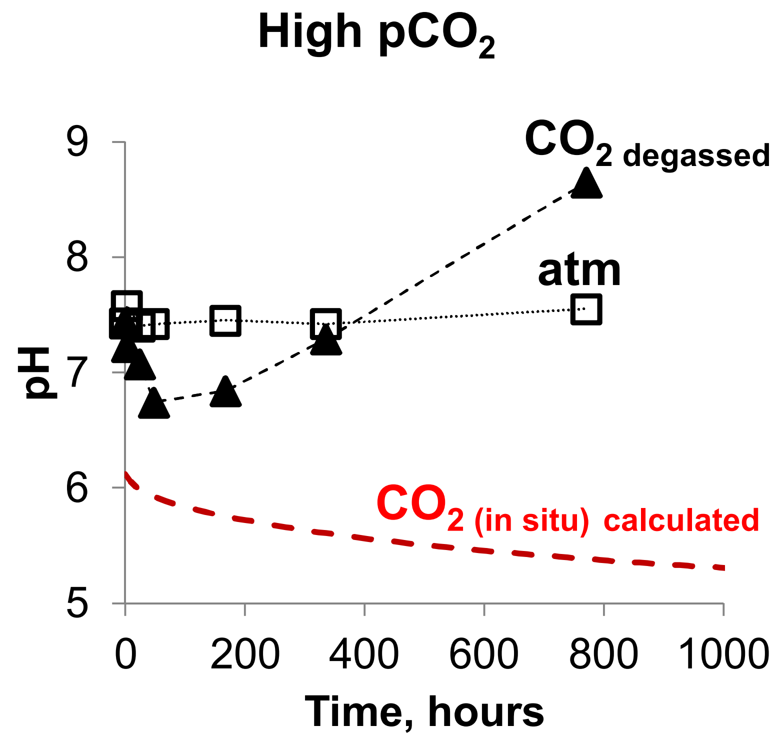


- Estimated solubility of CO_2 in brine = 0.84 M***

* Developed based on the dataset from "Natural Contamination from the Mancos Shale" Report, US DOE, ESL−RPT−2011−01.
** Accounting for mineral dissolution reactions.
*** Using Duan and Sun (2003) data for NaCl.

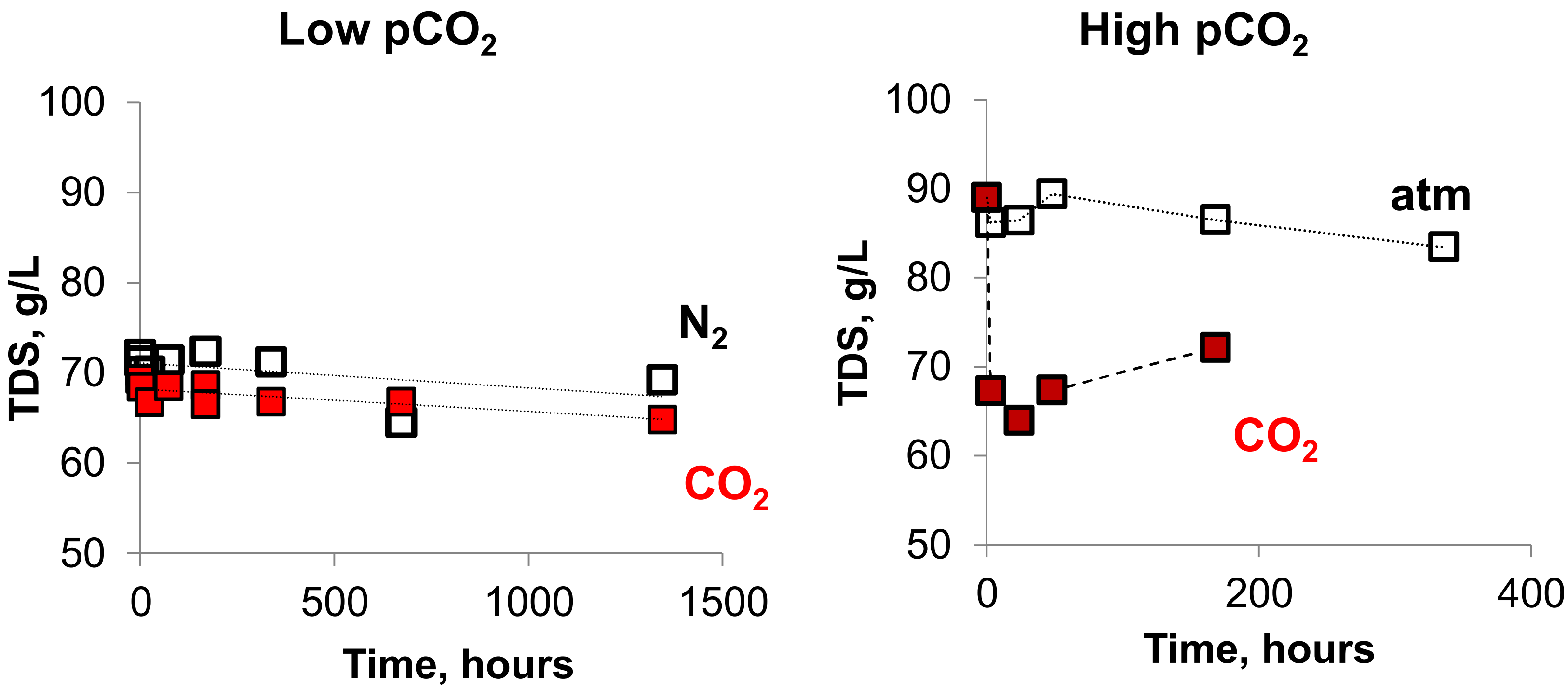
Aqueous chemistry: Mancos





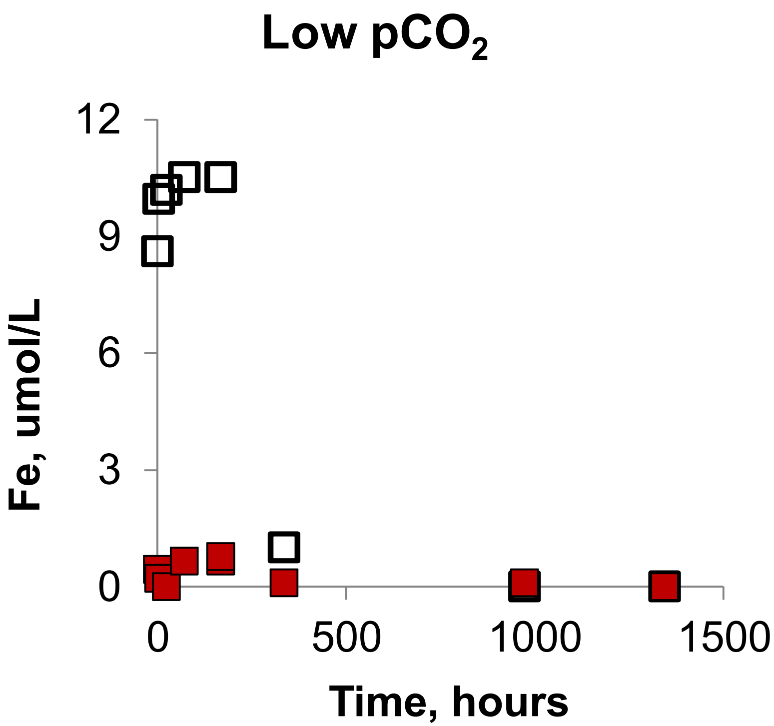
- pH is buffered by the dissolution of CO_2 into brine, and dissolution of carbonates.

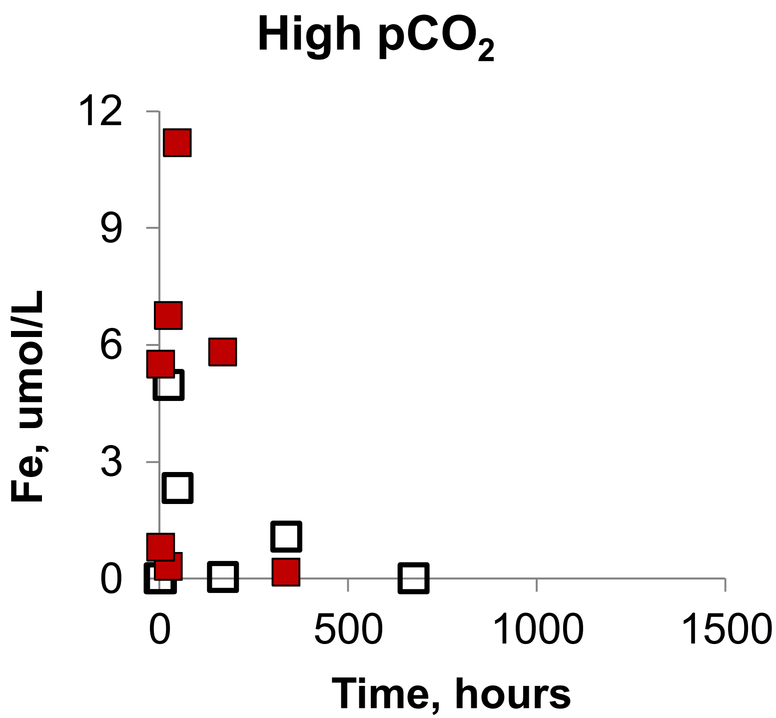
Aqueous chemistry: Mancos



- Decrease in TDS in low and high pCO_2reactors, and control reactors.
- Ca and Sr are more soluble in high pCO_2 vs. control reactors.

Aqueous chemistry: Mancos





- Very low (microM) Fe - Fe is more soluble in high p-CO_2 -pressurized reactor.
- Al – below the detection limit.

Aqueous chemistry: Mancos

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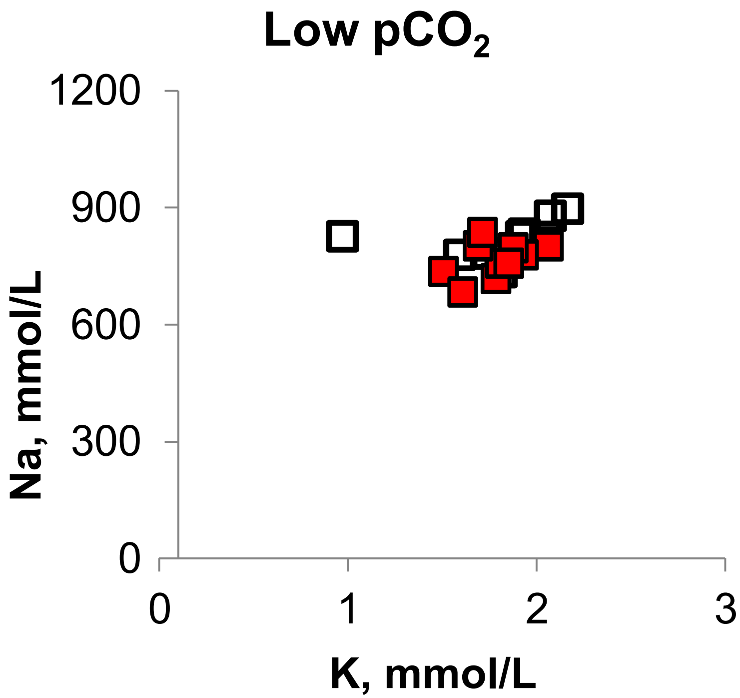
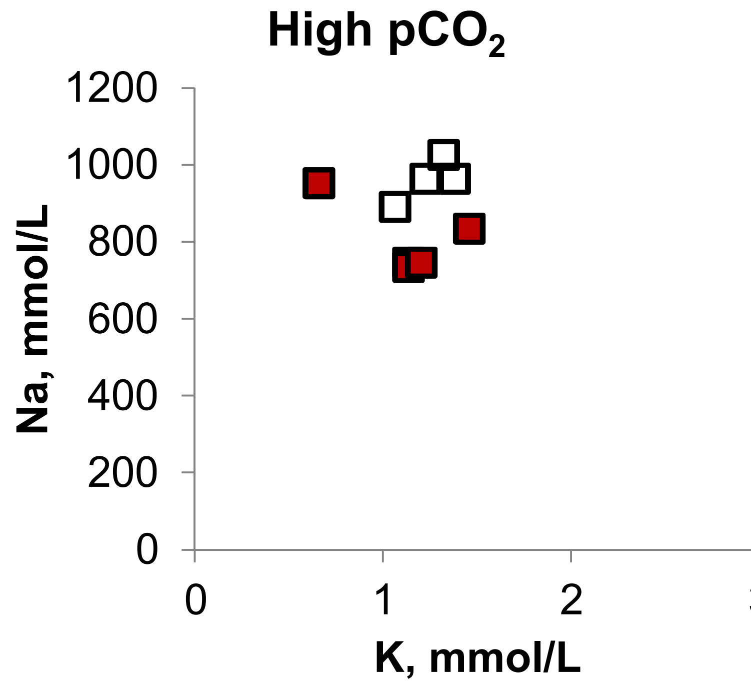
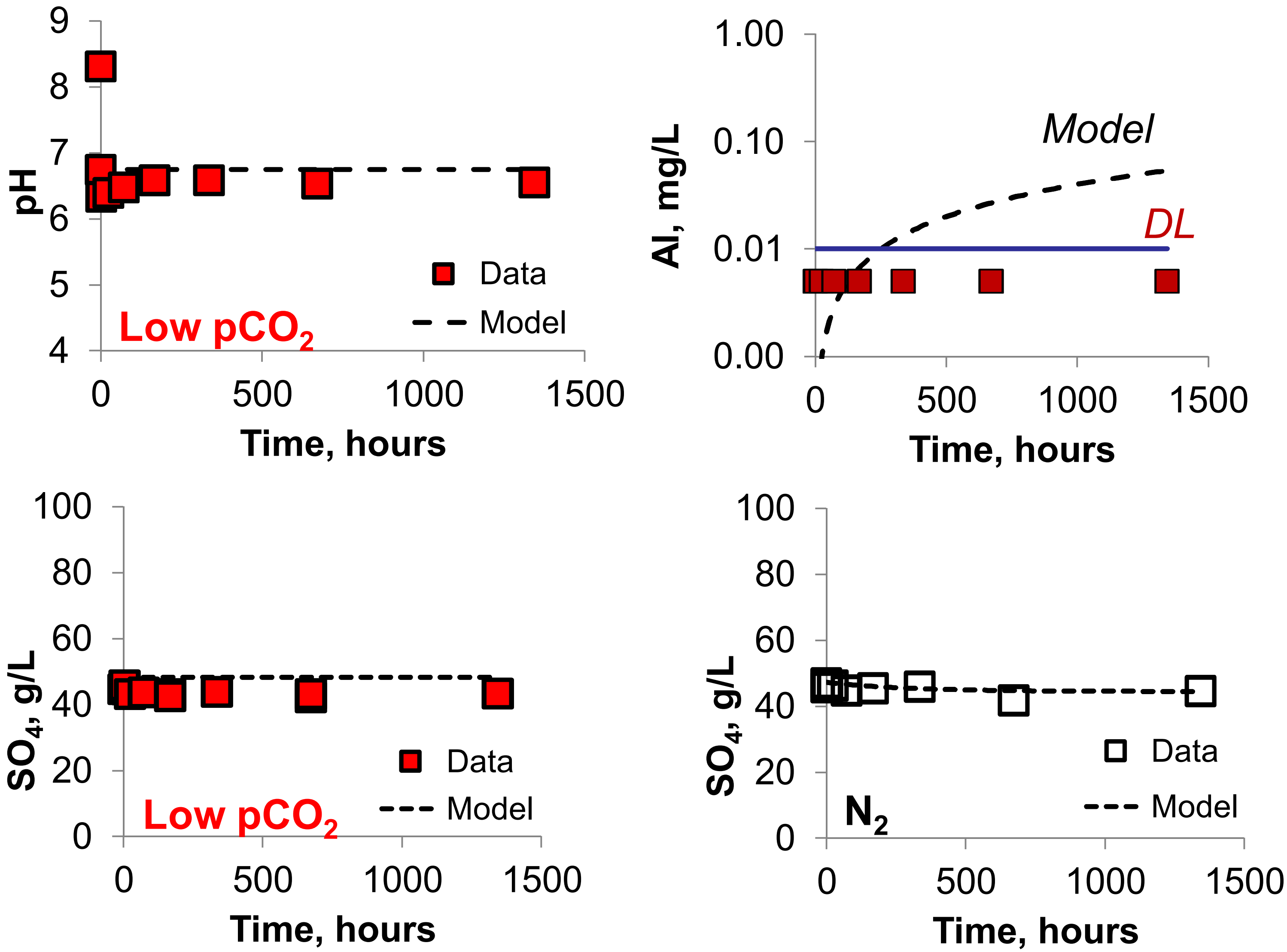




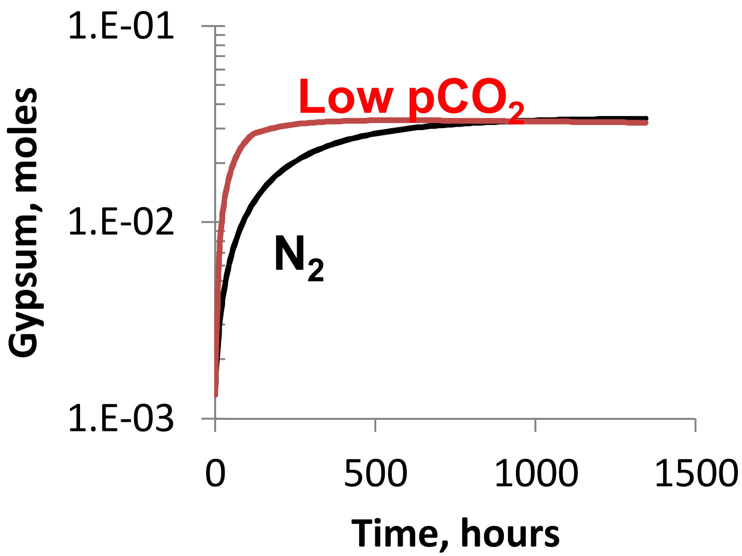
- Positive Na-K correlation indicates no cation exchange.

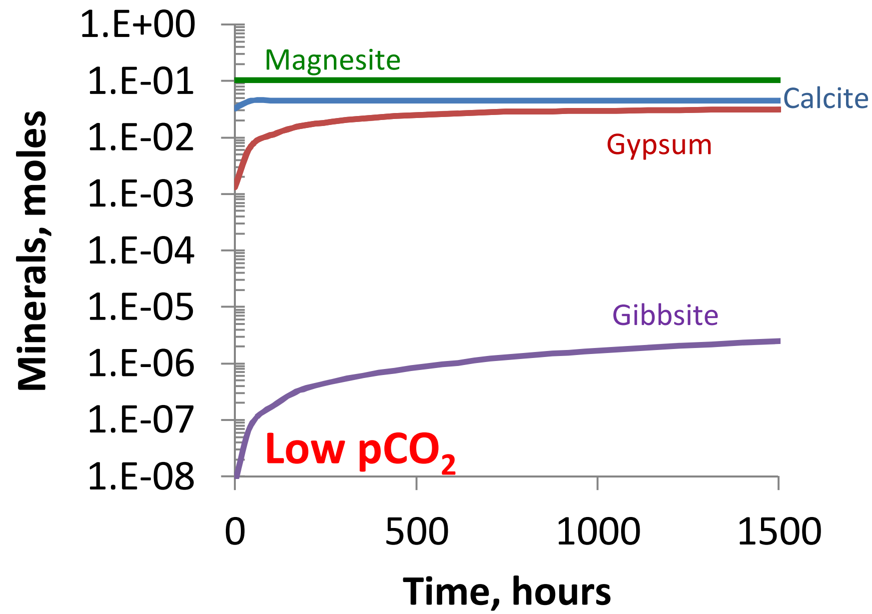
Geochemical modeling: Mancos

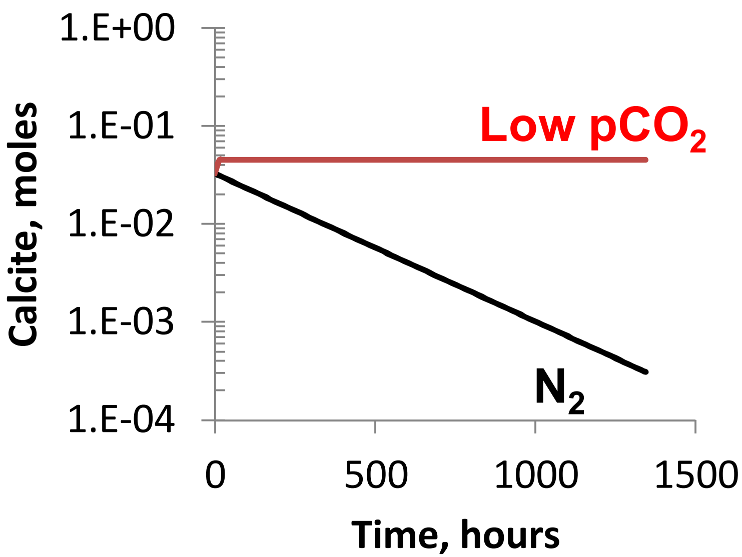


- Geochemical models capture major trends, but not everything (yet!).

Geochemical modeling: Mancos

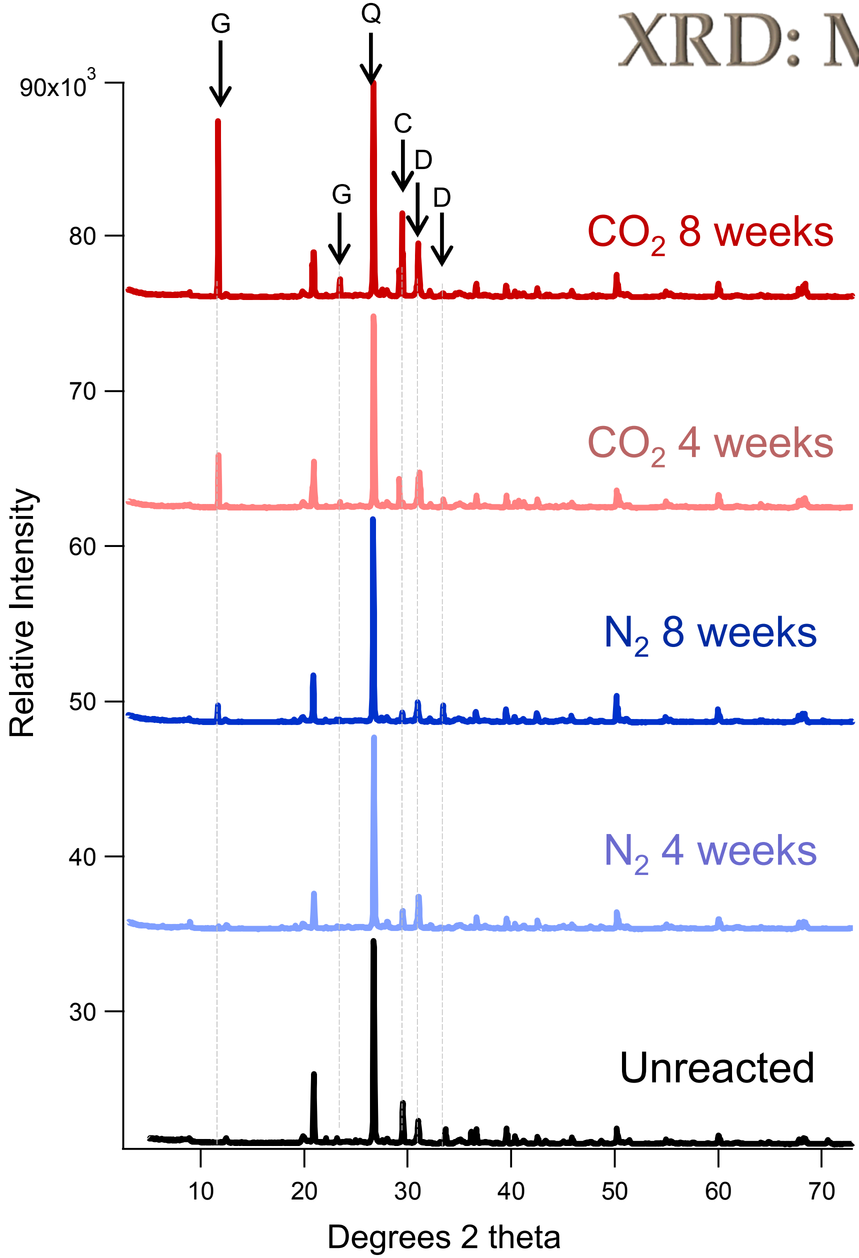




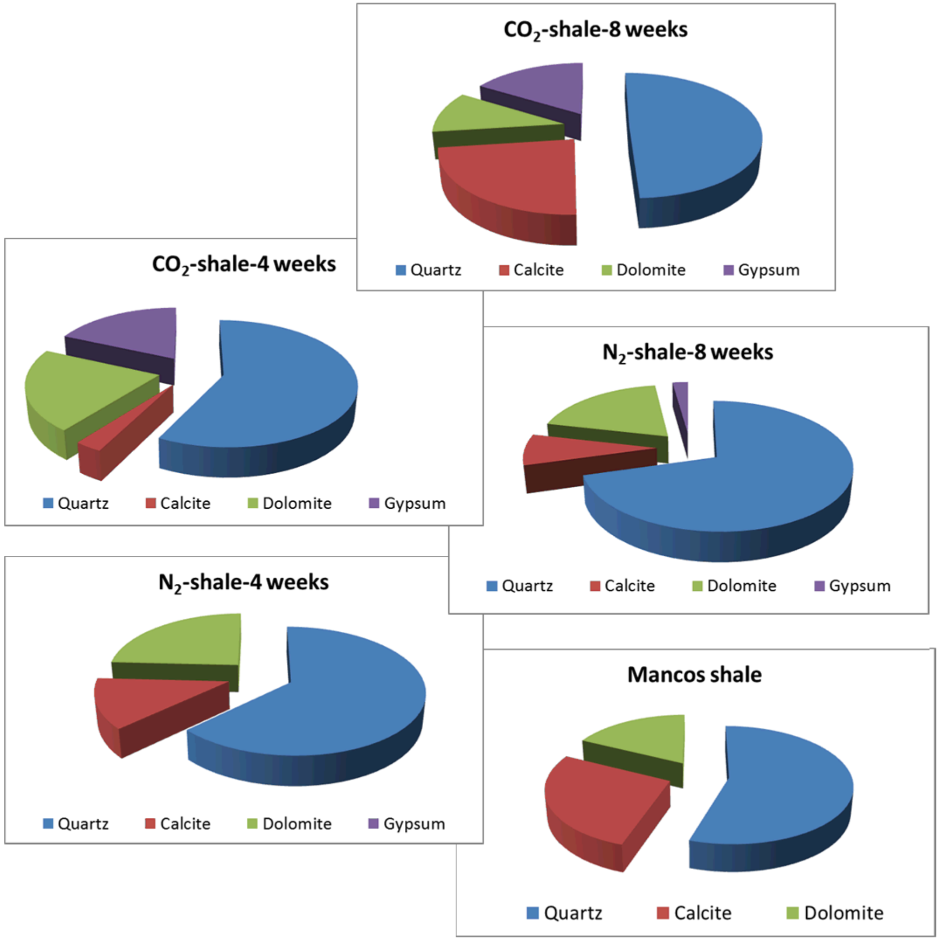


- Calcite dissolution/ precipitation and gypsum precipitation are the predominant mineralogical changes on the time scale of the experiment.
- Model predicts: minor amount of brucite in N_2-pressurized reactor, and magnesite and gibbsite– in CO_2-pressurized reactor.

XRD: Mancos

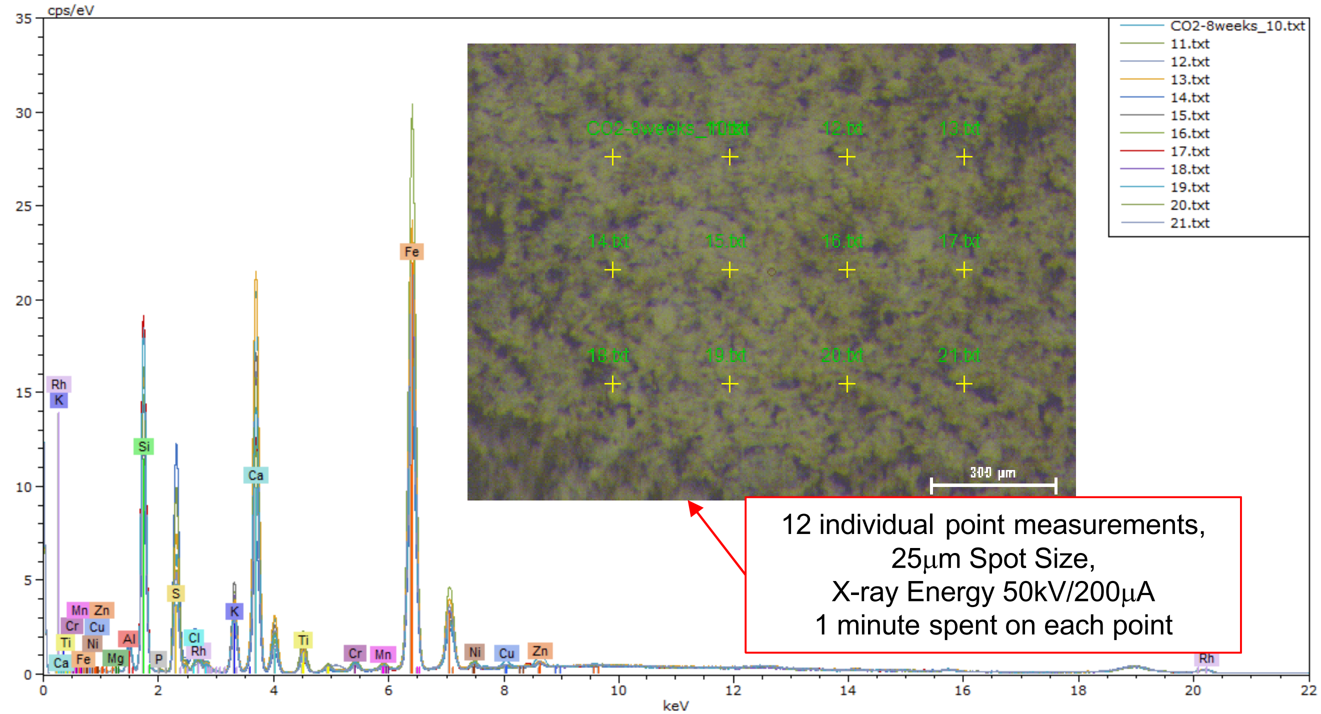


90x10^3
80
70
60
50
40
30
Relative Intensity
10
20
30
40
50
60
70
Degrees 2 theta
G
Q
G
C
D
D
CO2 8 weeks
CO2 4 weeks
N2 8 weeks
N2 4 weeks
Unreacted



CO2-shale-8 weeks
Quartz
Calcite
Dolomite
Gypsum
CO2-shale-4 weeks
Quartz
Calcite
Dolomite
Gypsum
N2-shale-8 weeks
Quartz
Calcite
Dolomite
Gypsum
N2-shale-4 weeks
Quartz
Calcite
Dolomite
Gypsum
Mancos shale
Quartz
Calcite
Dolomite

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

Mancos shale: Conclusions

$$CaCO_{3(s)} + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$$
calcite

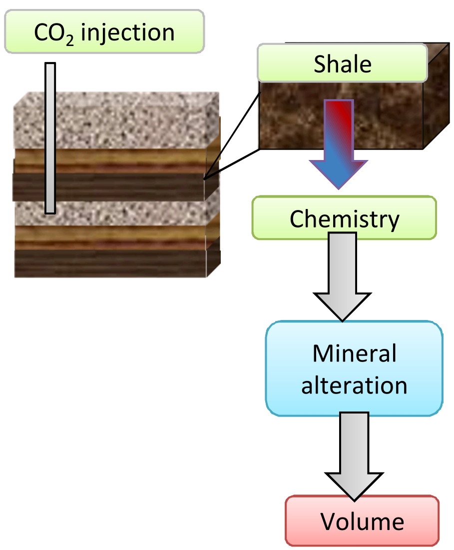
$$CaMg(CO_3)_{2(s)} + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2CO_3$$
dolomite

$$Mg^{2+} + H_2CO_3 \rightarrow MgCO_{3\,(s)} + 2H^+$$
magnesite

$$Ca^{2+} + H_2CO_3 \rightarrow CaCO_{3\,(s)} + 2H^+$$
calcite

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_{4\,(s)} + 2H^+$$
gypsum

$$KAl_3Si_3O_{10}(OH)_{2(s)} + 4H_2O \rightarrow 3Al(OH)_{3(s)} + 3SiO_2 + K^+ + OH^-$$
muscovite, gibbsite



Mineral	Calcite	Albite	Dolomite	Muscovite
ρ, 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**
ρ, g cm^{-3}	2.71	2.3	3	2.42
Hardness	3	2	4	3

Alteration by CO_2-brine mixture maybe causing net decrease in density and hardness.

Fracture Toughness: Scratch Test

$$K_c = \frac{F_T}{\sqrt{2pA}} \text{ [Mpa*m}^{1/2}\text{]}$$

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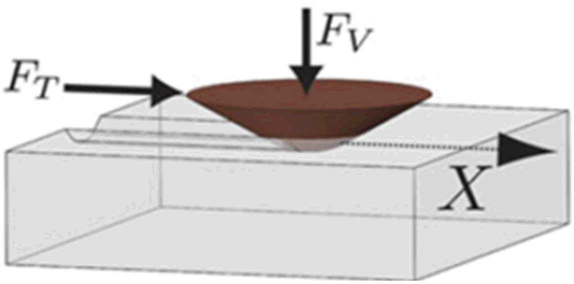
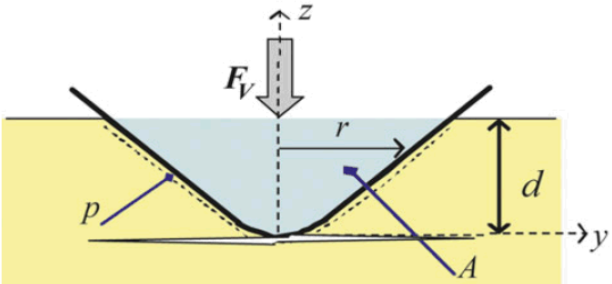
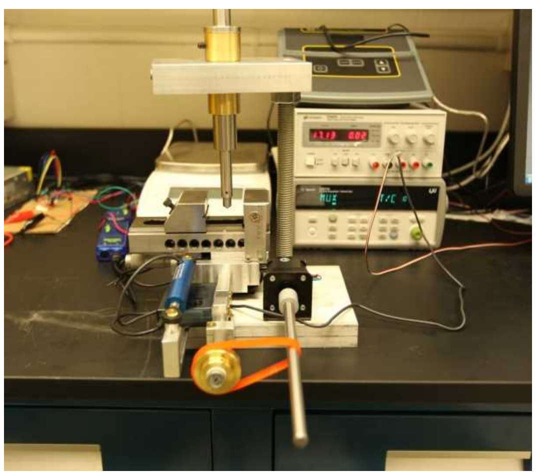
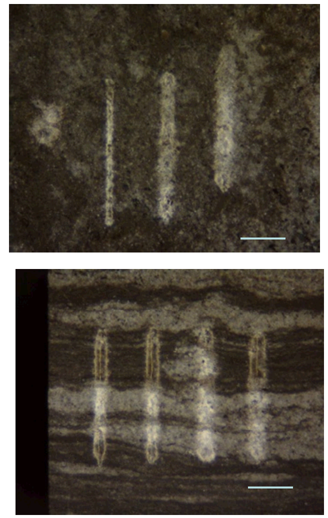


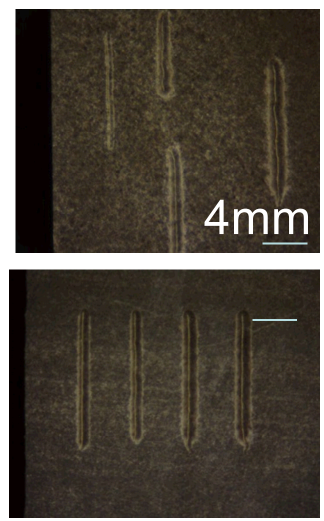


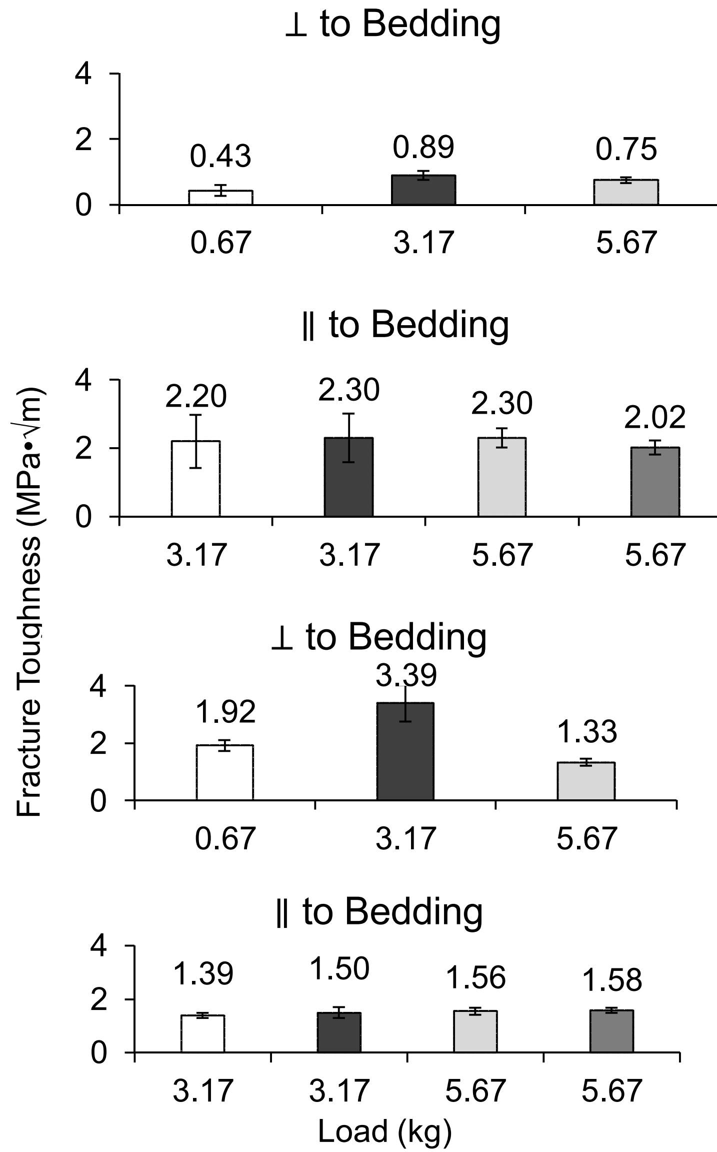


Mancos Shale



Woodford Shale

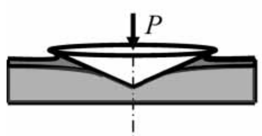




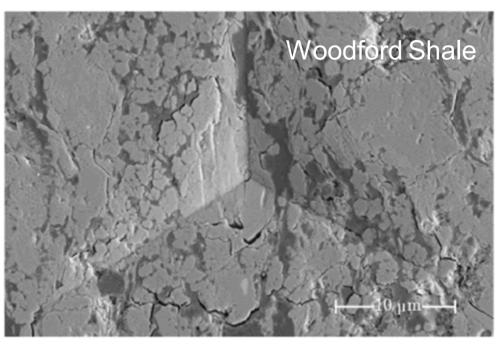
Micromechanical Properties

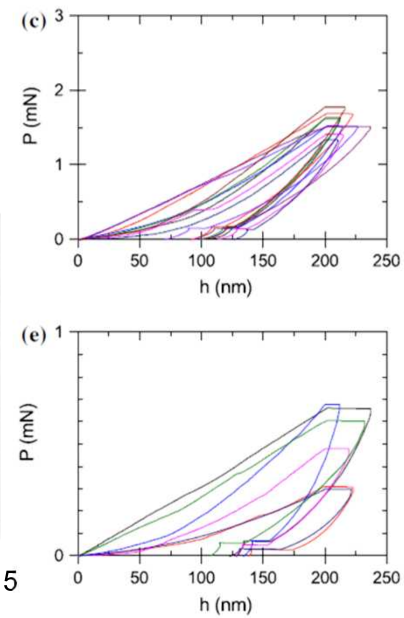
Micron scale laboratory experiments on unaltered and chemically altered shales to assess changes in mechanical properties like hardness, Young's Modulus, and unconfined compressive strength due to chemical reactions likely to occur with $scCO_2$ in GCS. Results can be applied to assess long-term caprock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

Nano-indentation	Micropillar compression
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.	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.

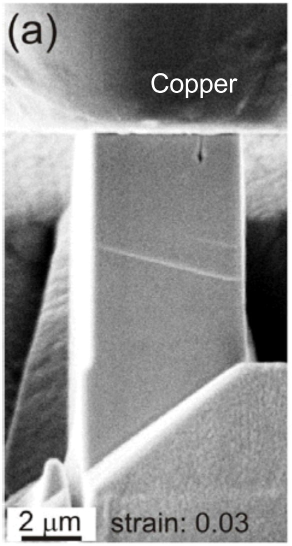


Tang & Ngan, 2007

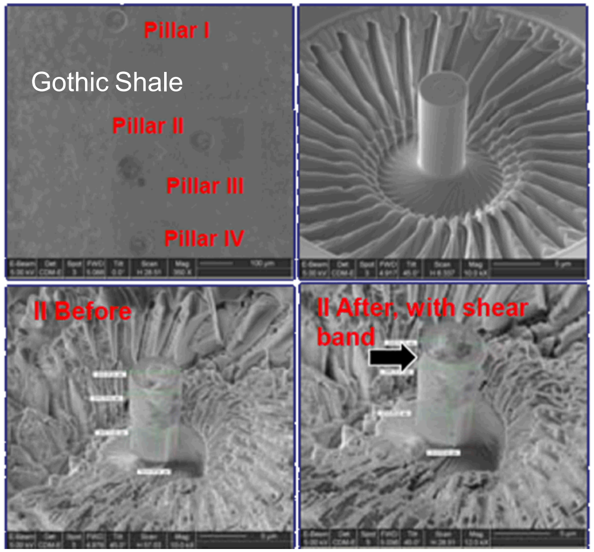




Bennett et al., 2015



Kiener et al., 2011



Dewers et al., 2010

Acknowledgements

People

Mona Aragon, SNL – CO_2 injection graphics

Funding

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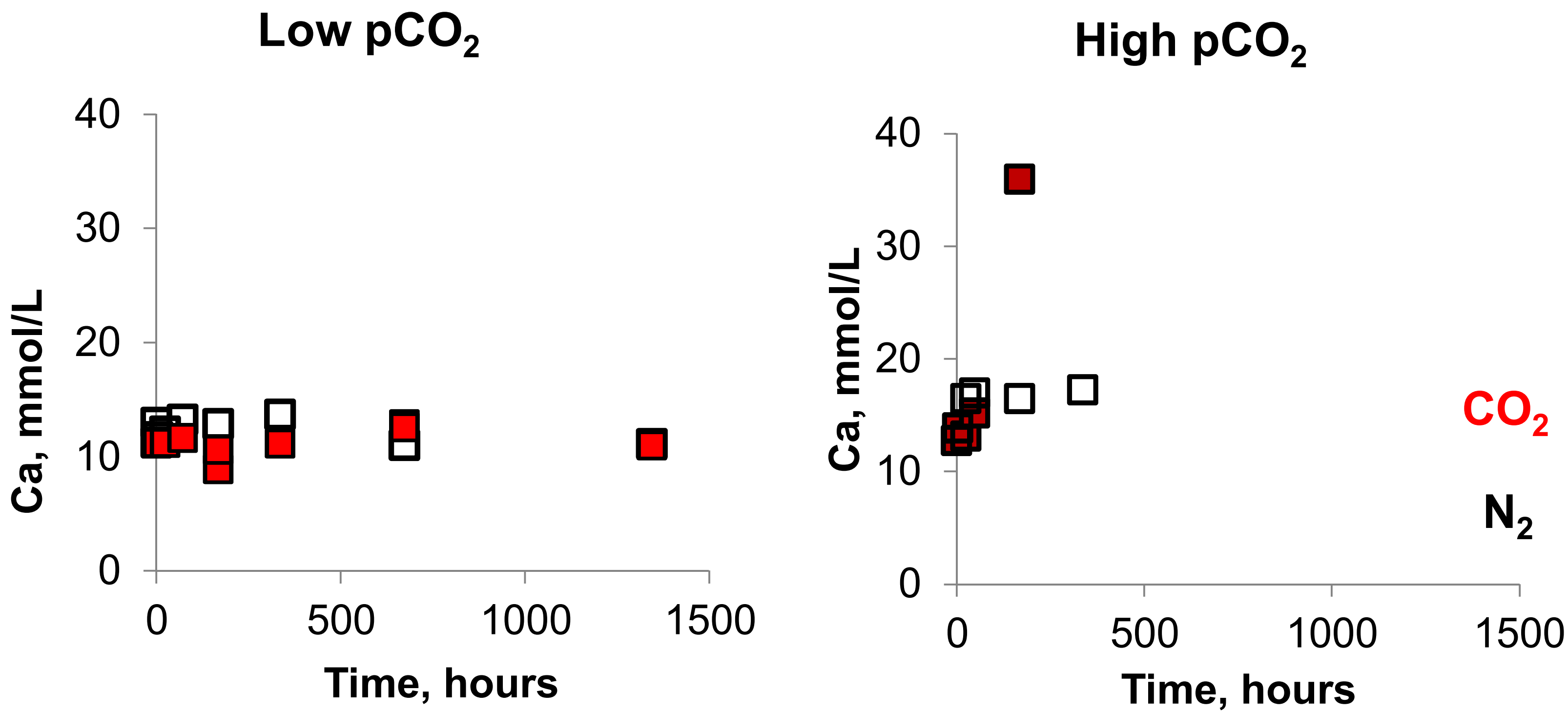
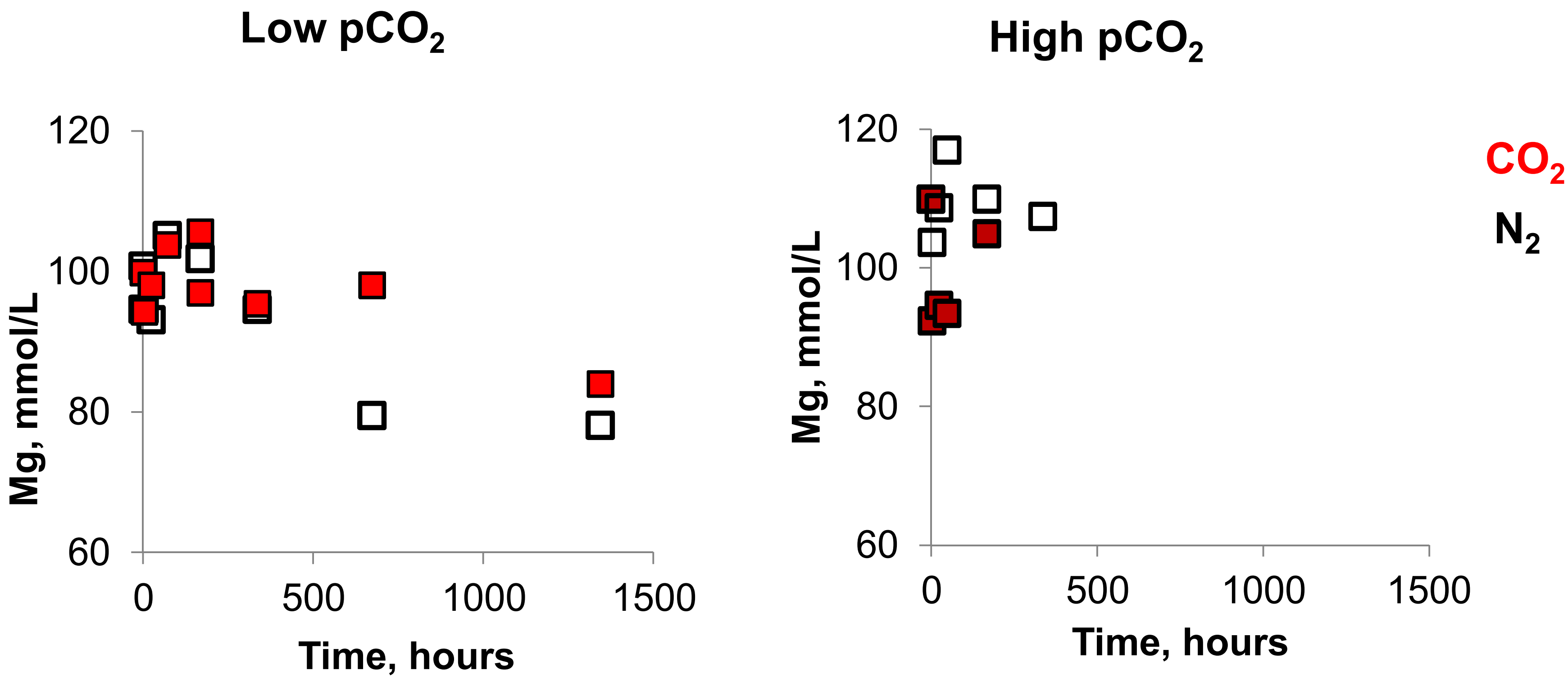
Extra slides

Aqueous chemistry: Mancos



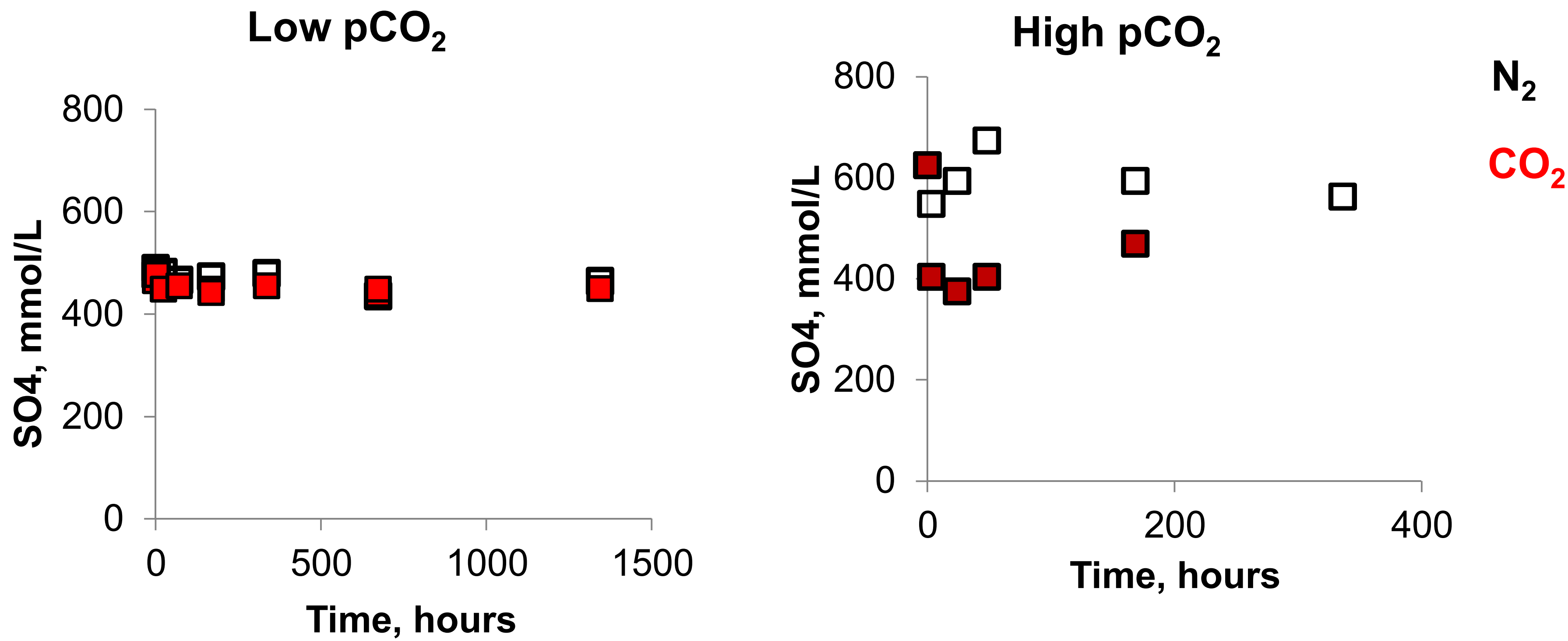
- Ca is more soluble in high p-CO_2 -pressurized reactor

Aqueous chemistry: Mancos



- Ca, Mg, Si, Sr, and Fe are more soluble in CO_2 vs. N_2 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.