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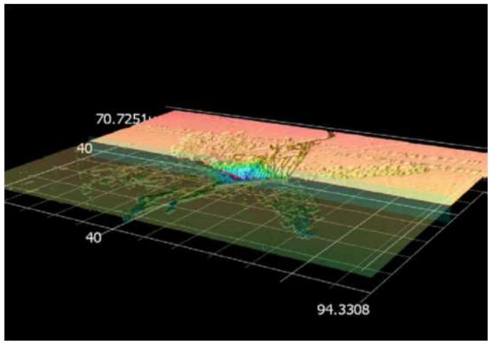

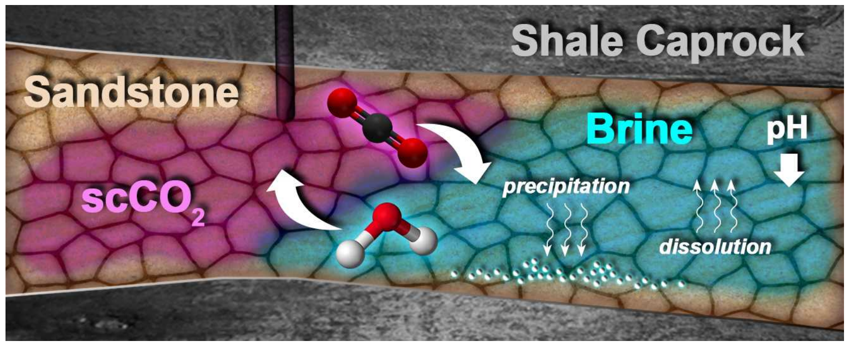

Shale-brine-CO_2 interactions and the long-term stability of carbonate-rich shale caprock

Anastasia Ilgen, M Aman, DN Espinoza, MA Rodriguez, JM Griego, TA Dewers, JD Feldman, TA Stewart, and RC Choens

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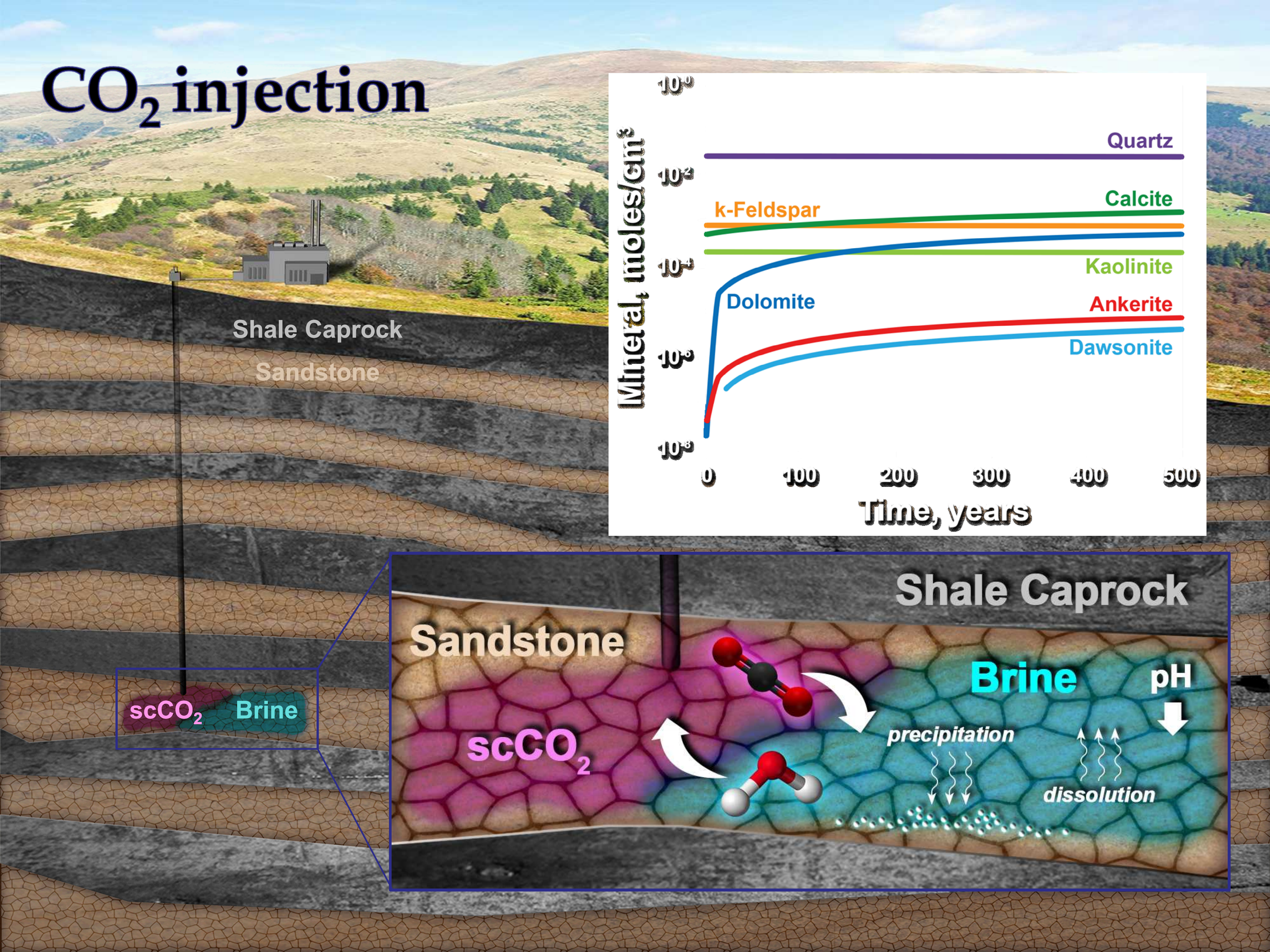

CO2 injection
Shale Caprock
Sandstone
scCO2
Brine
Mineral, moles/cm3
10-0
10-2
10-4
10-6
10-8
0
100
200
300
400
500
Time, years
Quartz
Calcite
k-Feldspar
Kaolinite
Dolomite
Ankerite
Dawsonite
Shale Caprock
Sandstone
Brine
pH
scCO2
precipitation
dissolution

Geochemical response triggered by the injection of CO_2

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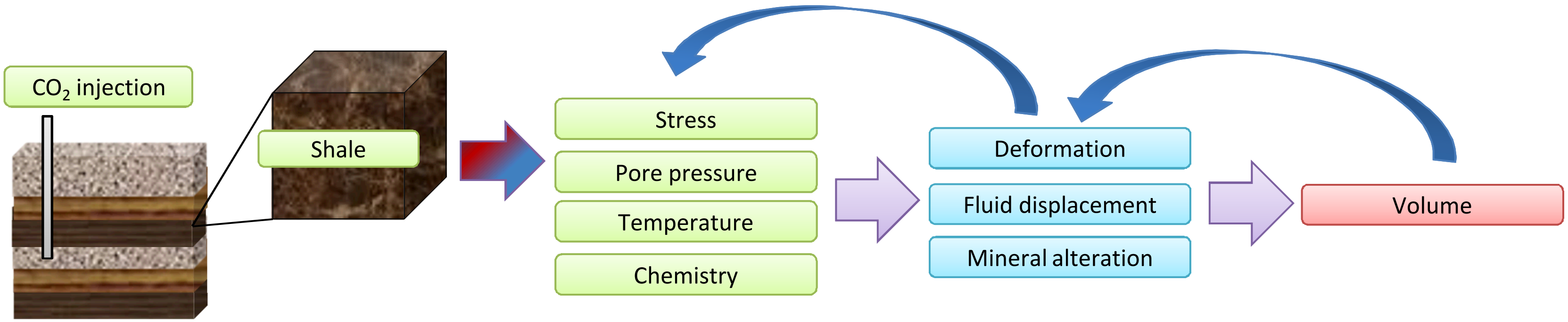
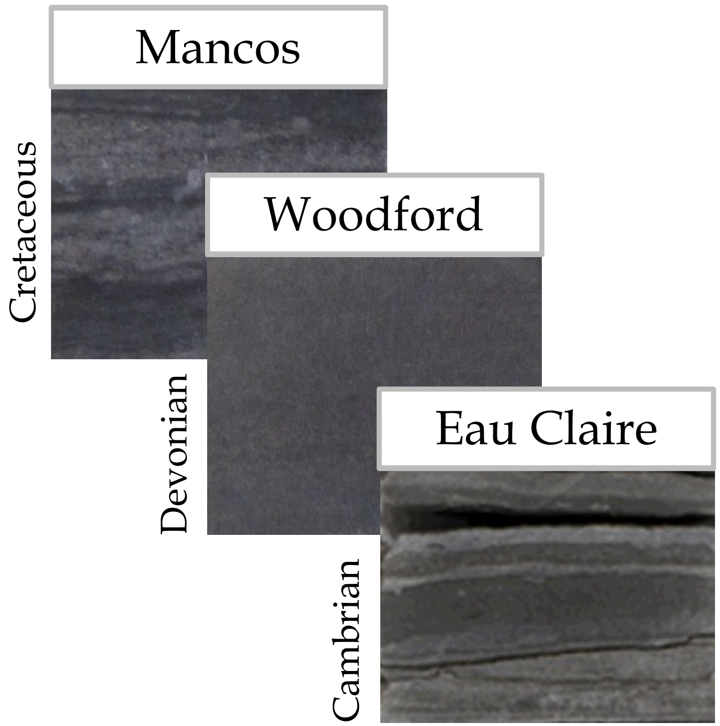
- At geologic storage PT: CO_2 is supercritical ($scCO_2$).
- $scCO_2$ stimulates **geochemical responses**: acidification of parent brine, and dehydration of mineral surfaces.[1-3, 8]
- Experimental and field studies: geochemical reactions differ significantly for different rock assemblages and brine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

Objectives

Establish quantitative relationships between chemical reactions triggered by the addition of supercritical CO_2 and changes in 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.

- 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

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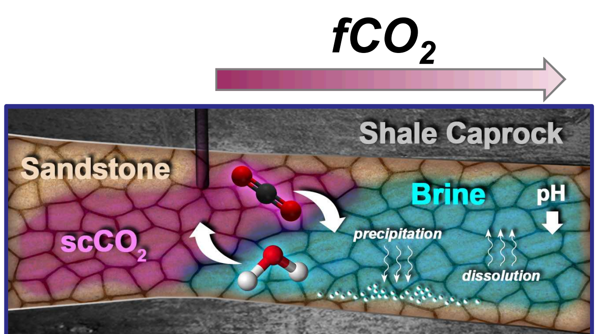


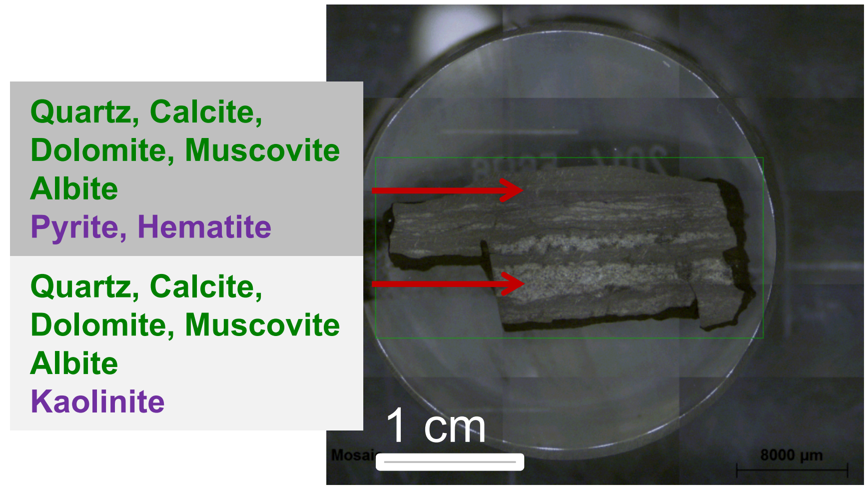
- Stirred reactors pressurized with CO_2
- Control reactors – pressurized with N_2 or buffered by ambient atm
- Powdered shale (A_{BET} = 8.3 m^2 g^{-1}) + brine
- Sample brine and solids at time intervals
- Analysis by IC, ICP-MS, and XRD
- Geochemical modeling

Mancos shale alteration in brine-CO_2 mixtures

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

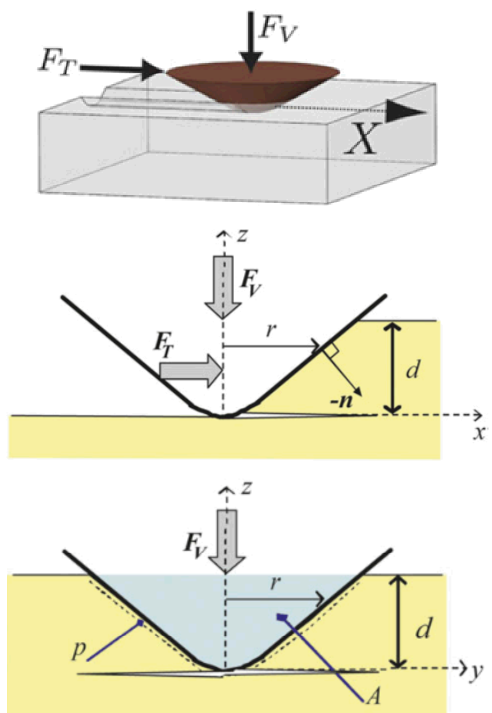


- Estimated solubility of CO_2 in brine = 0.84 M***

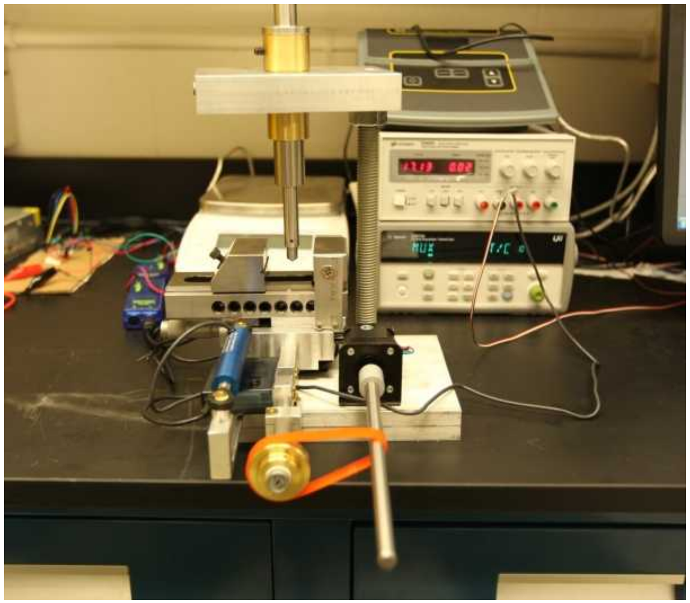
* Developed based on the dataset from "Natural Contamination from the Mancos Shale" Report, US DOE, ESL−RPT−2011−01.
** Accounting for mineral dissolution reactions.
*** Using Duan and Sun (2003) data for NaCl.

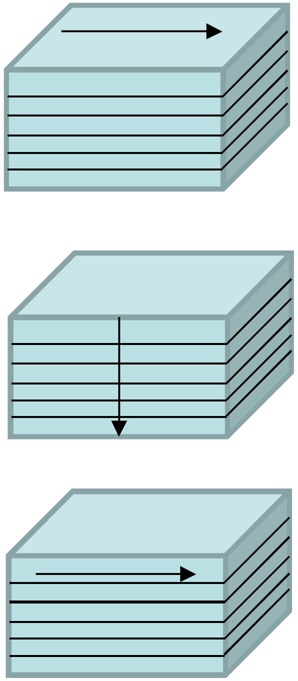
Micro-scratch testing

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



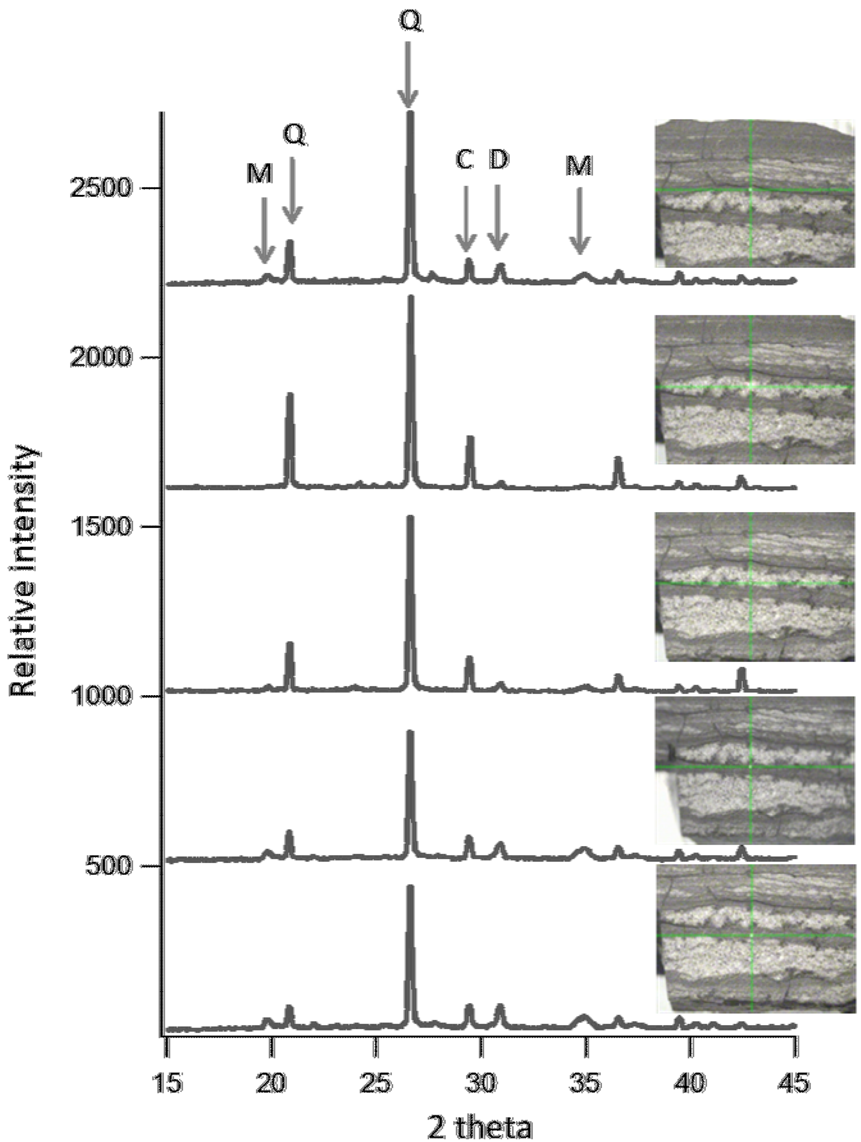
[1] Akono and Randall, 2012

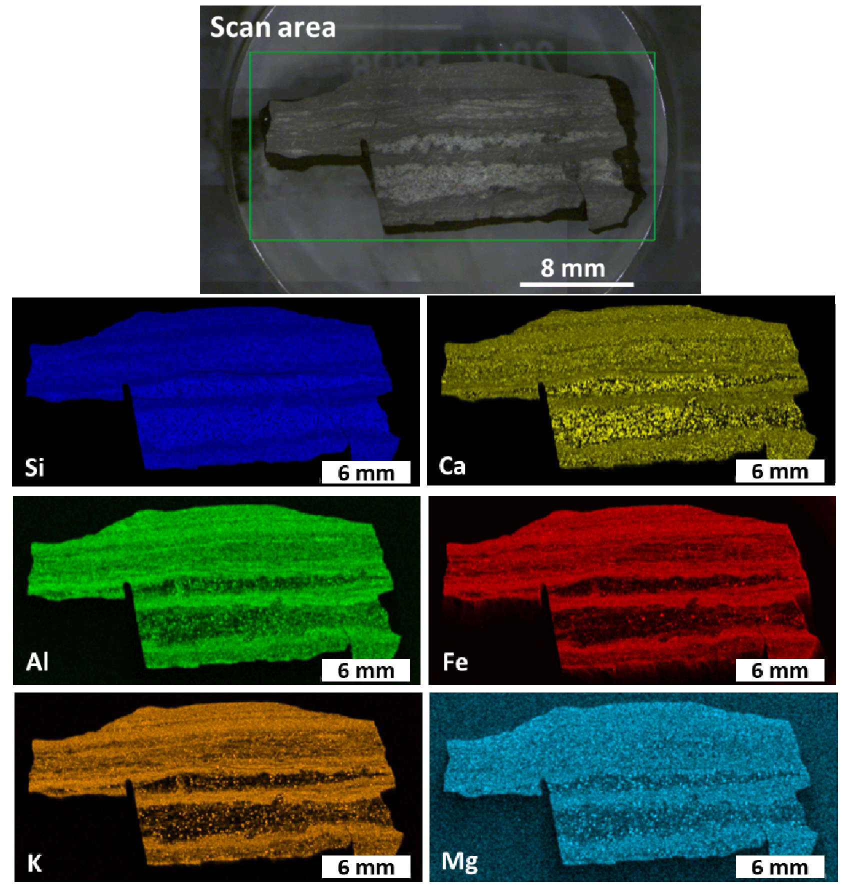




- Scratching directions
  - Parallel to bedding
  - Perpendicular to bedding:
    - Against lamination – Scratch crosses bedding planes
    - With lamination – Scratch travels along the bedding plane

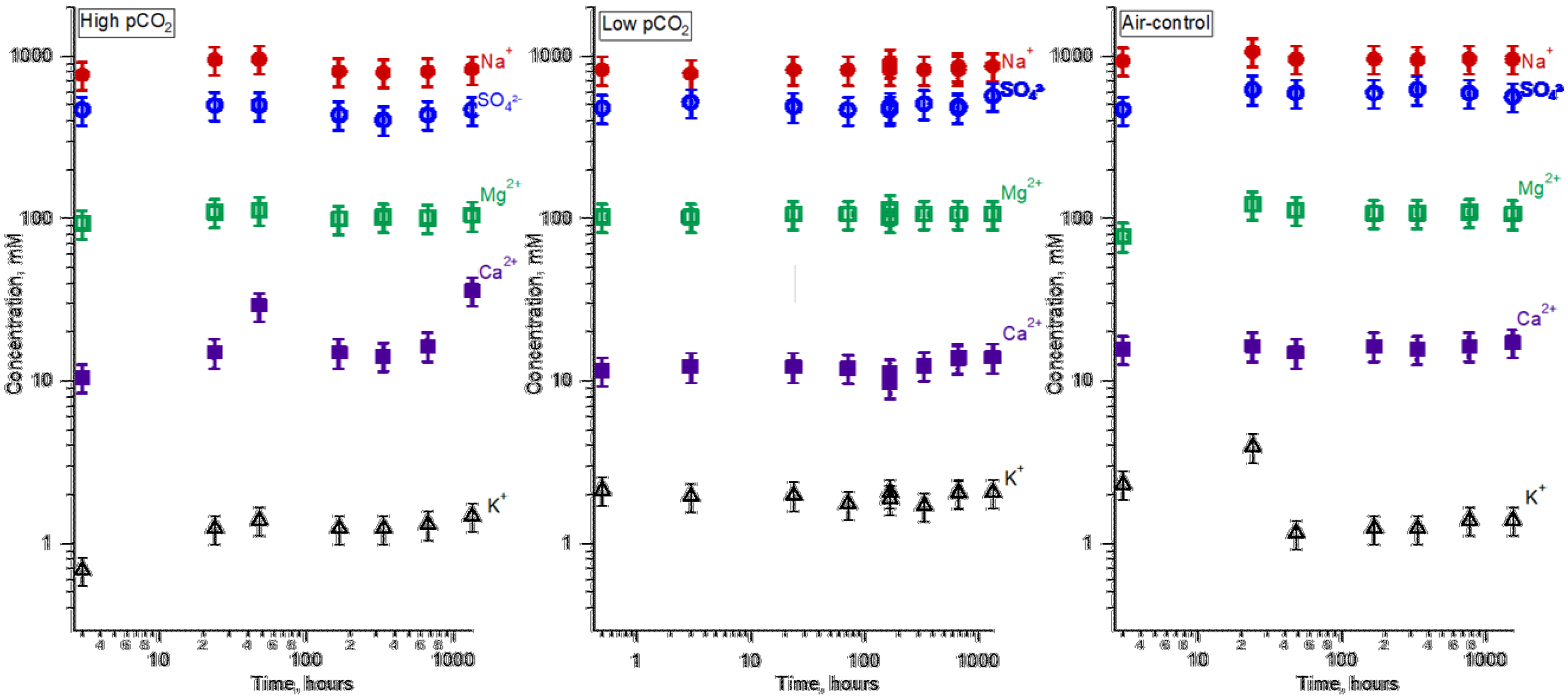
Characterization of heterogeneity





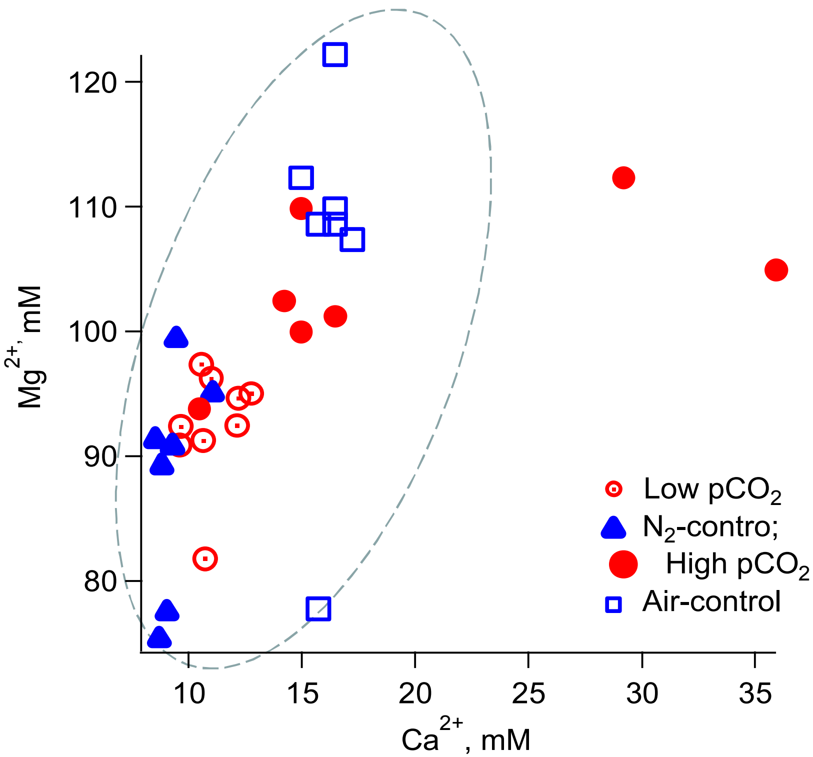
- μXRD shows the peak intensities of dolomite and muscovite lower in the lighter layers, and higher peak intensity for calcite. This is supported by the μXRF elemental maps.

Aqueous chemistry: Mancos



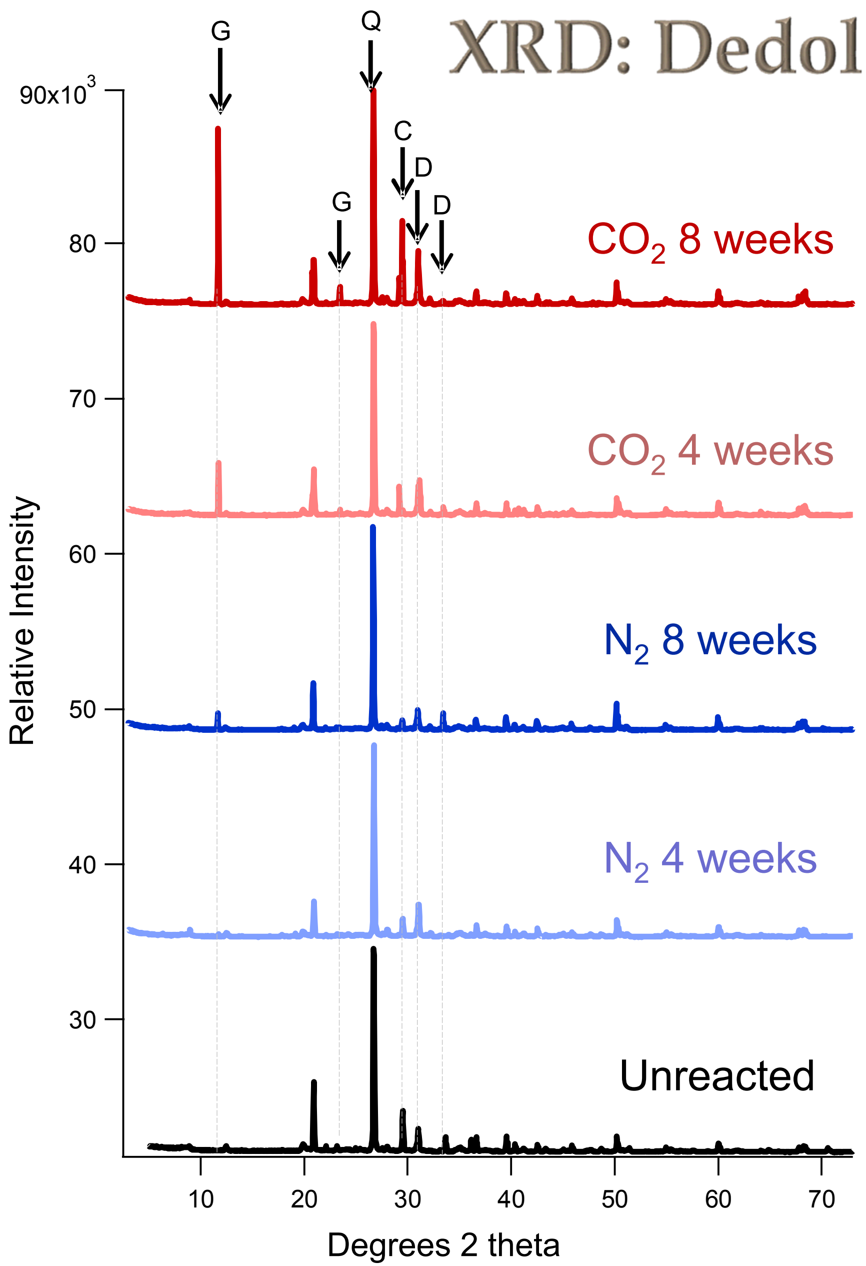
- Release of Ca, due to the dissolution of calcite, Mg, due to the dissolution of dolomite, and release of K, due to the dissolution of muscovite, or, potentially, illite, were observed. These elements were released to a larger degree in the high pCO_2 reactor, compared to the control and low pCO_2 reactors;
- Low mobility of aluminum and iron in all reactors.

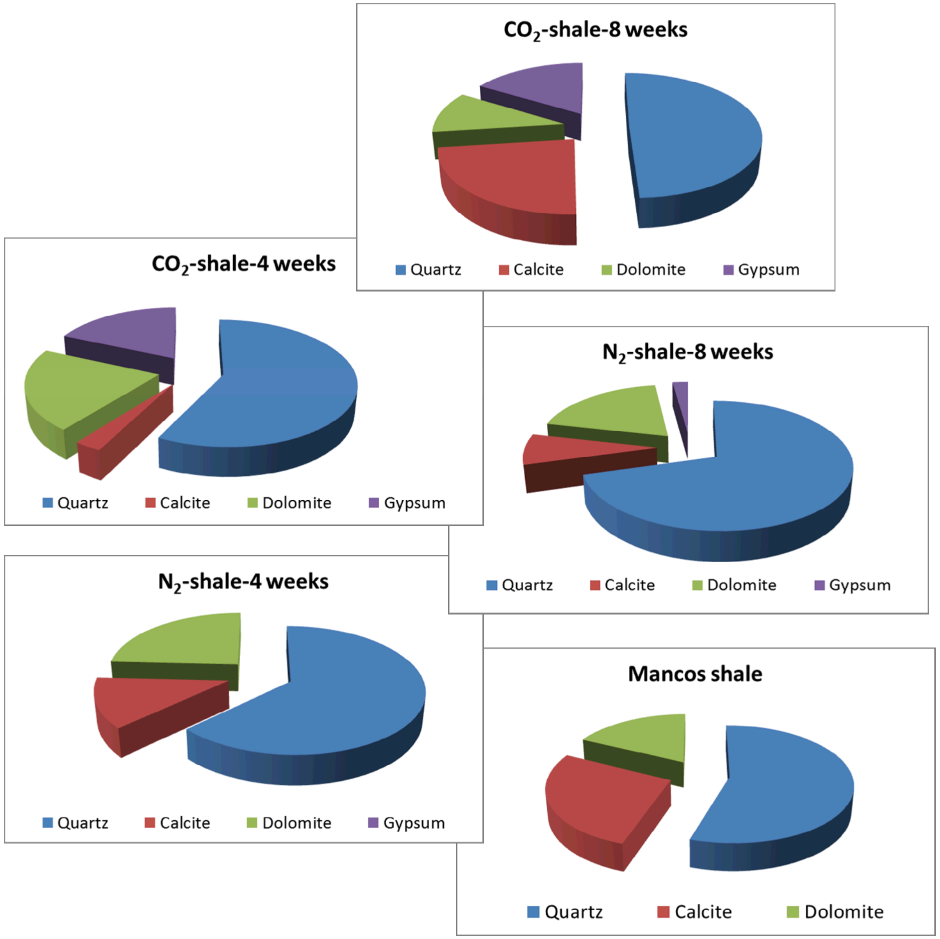
Dolomite dissolution



- Positive correlation between Ca and Mg observed in high and low pCO_2 reactors, and in Air- and N_2-control reactors.

XRD: Dedolomitization





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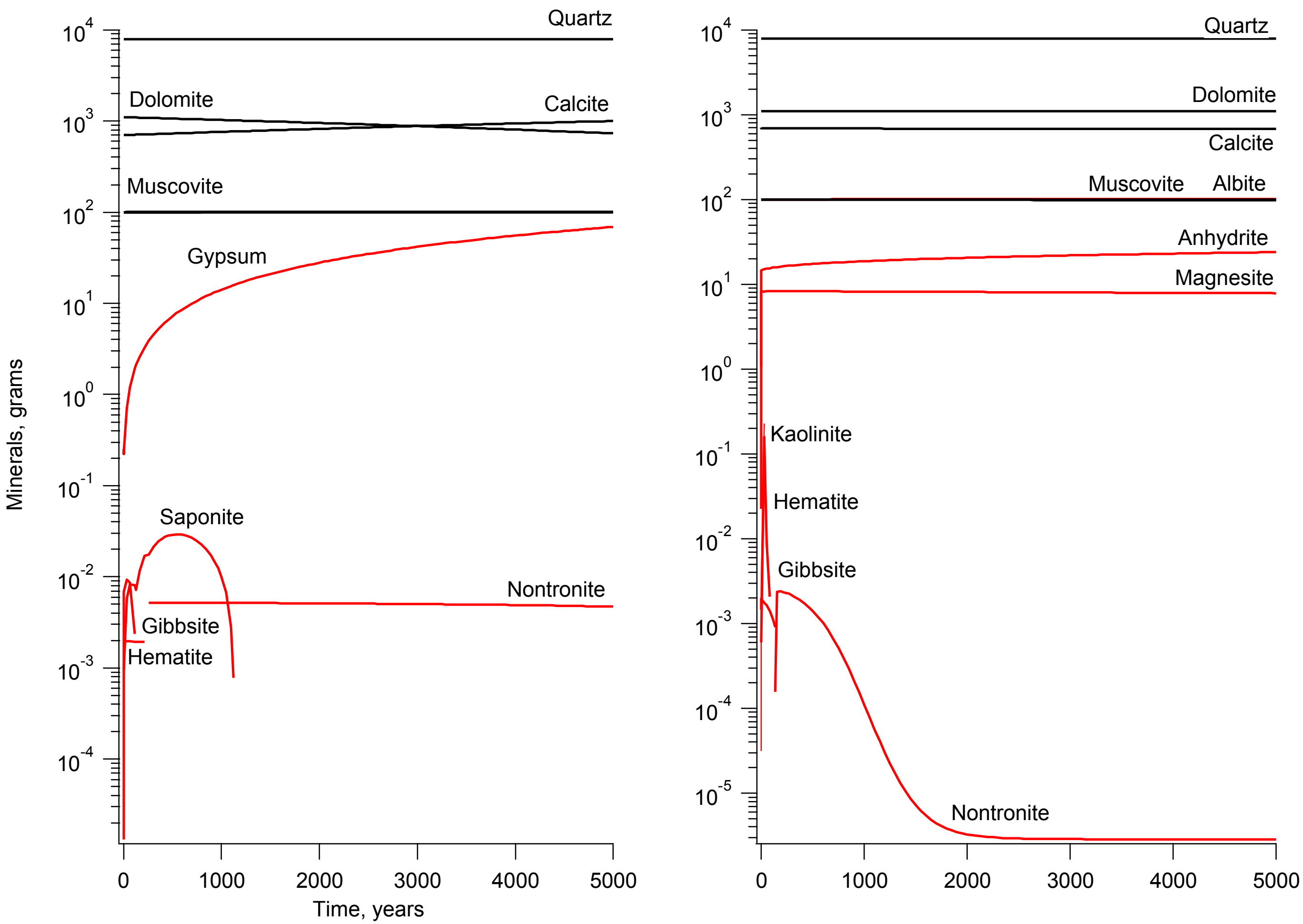
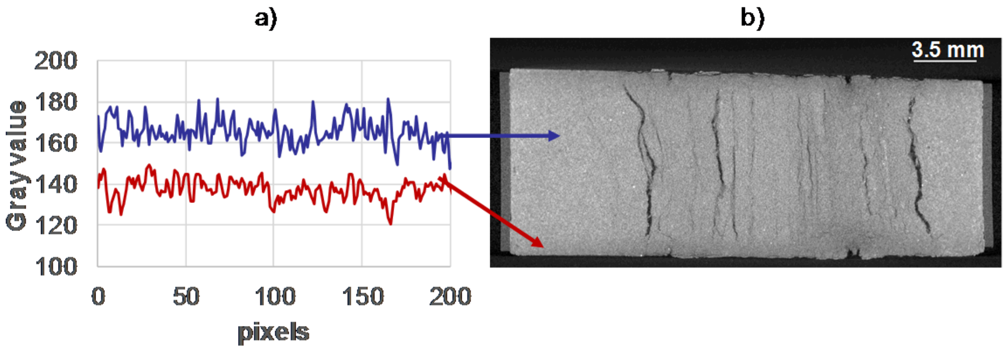
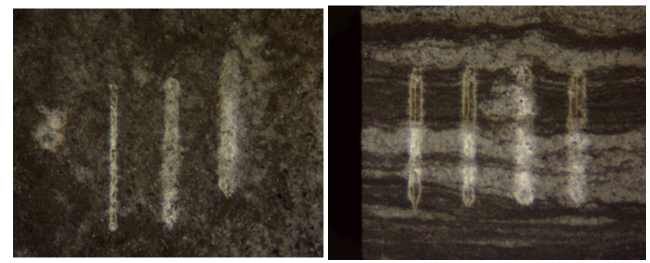
Geochemical modeling

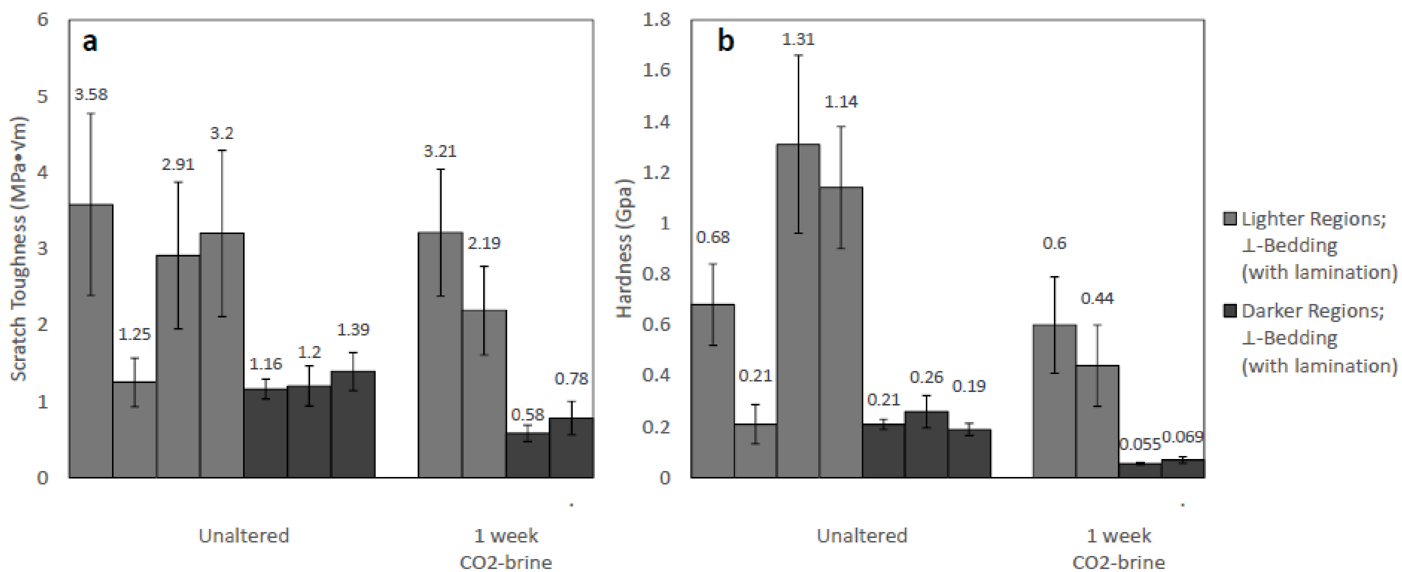


- Geochemical modeling: (a) low pCO_2, and (b) high pCO_2. Minerals included in the model are shown in black, and secondary minerals are shown in red.

Fracture Toughness: Scratch Test







- The quartz-rich, high hardness regions of Mancos shale did not show significant changes in the scratch toughness following the alteration for one week in CO_2-brine mixture.
- Decrease in scratch toughness of about 50% on the darker (dolomite- and muscovite-rich) softer regions.

Chemical and mechanical alteration of natural carbonate-rich shale

Low pCO_2 reactor:

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

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

$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O_{(s)}$

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

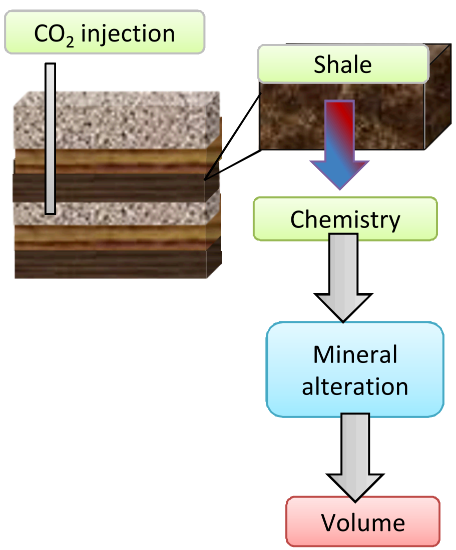
High pCO_2 reactor:

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

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

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

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



- CO_2 pressure-dependent mineralogical changes.
- Dedolomitization in the low pCO_2 reactor, with initial dissolution of calcite, followed by the replacement of dolomite with calcite and precipitation of gypsum.
- Complete dissolution of calcite, partial dissolution of dolomite, and precipitation of magnesite and anhydrite in the high pCO_2 reactor.
- The micro-mechanical testing indicated localized mechanical weakening. The decrease of up to 50 ± 20 % in calculated scratch toughness was observed for the dolomite- and muscovite-illite enriched laminae.
- The geochemical models predict limited mineralization and alteration after 5,000 years, with minor shifts in the bulk density and hardness.

If CO_2 reaches a carbonate-rich layered shale caprock, it would likely migrate laterally along the more susceptible shale lamina. Dedolomitization may be an important process since it could cause changes in porosity and permeability, affecting the development of preferential flow paths.

Acknowledgements

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People

Mona Aragon, SNL – CO_2 injection graphics

Funding

- **Laboratory Directed Research and Development, Sandia National Laboratories.**
- **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.**

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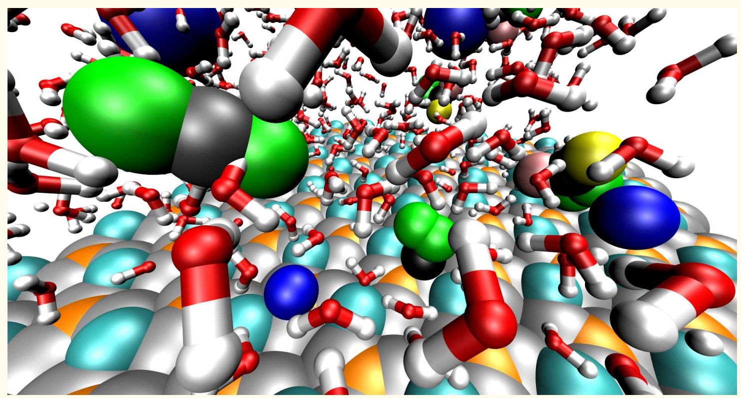
Science of Carbon Storage in Deep Saline Formations

Process Coupling Across Time and Spatial Scales



Edited by
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Geochemical Modeling: Mancos

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

Table 1. Mineralogical composition of Mancos shale, dissolution rate constants, and composition of synthetic brine used in the batch reactors. The specific surface areas were set at 1 cm^2 g^{-1} for all minerals in geochemical models.

Minerals			**Synthetic Brine** [b)]	
Mineral	**wt.%**	**k, mol cm^{-2} sec^{-1}**	pH = 7.44	
Quartz	82 (79) [a)]	1×10^{-17}	I = 1.3 M	
Calcite	6.7 (7)	1×10^{-8}	Cl^-, mg L^{-1}	3300
Dolomite	11.3 (11)	1×10^{-12}	SO_4^{2-}, mg L^{-1}	47000
Albite	(1)	1×10^{-16}	K^+, mg L^{-1}	24.6
Muscovite	(1)	1×10^{-14}	Ca^{2+}, mg L^{-1}	455
Kaolinite	(1)	1×10^{-14}	Na^+, mg L^{-1}	18500
Pyrite	[c)]		Mg^{2+}, mg L^{-1}	2320
Hematite	[c)]		Fe^{2+}, mg L^{-1}	1.29
Rutile	[c)]			
Illite	[c)]			

Summary: XRD

Table 2. Semi-quantitative XRD analysis for high and low pCO_2 and control reactors.

Mancos sample	Quartz	Dolomite	Calcite	Thenardite	Halite	Gypsum	Anhydrite	Magnesite
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
Unreacted Mancos shale	82	11.3	6.7					
Low pCO2								
Low pCO_2-4weeks	57.6	21.2	2.9			18.3		
Low pCO_2-8weeks	49.4	10.7	23.5			16.3		
High pCO2								
High pCO_2-4weeks	70.6	11.8			1.1		15.9	0.7
High pCO_2-8weeks	67.3	11.1		1.8	2.3		15.8	1.7
Control samples								
N_2-Control-4weeks	63	24.2	12.8					
N_2-Control-8weeks	70.6	19.2	8			2.2		
Air-Control-4weeks	80.1	9.3	5.4	2.7		2.4		
Air-Control-8weeks	45.2	13.2	4.8	30.8	6.1			

Geochemical Modeling: Mancos

Table 3. Summary of predicted changes in Mancos shale mineralogy, based on the geochemical modeling.

High pCO_2

Mineral	Mass, initial, g	Mass at 5,000 years, g	Density, g cm^{-3}	Hardness
Quartz	7900	7900	2.62	7
Calcite	700	683	2.71	3
Dolomite	1100	1101	2.84	3.75
Kaolinite	100	102	2.6	1.75
Albite	100	99.7	2.62	7
Muscovite	100	98.0	2.82	2.25
Anhydrite	0	23.9	2.97	3.5
Magnesite	0	7.8	3	4
Nontronite	0	0.000003	2.3	1.75

	Initial	After 5,000 years
Rock mass, g	10,000	10,015
Average density	2.65	2.66
Average hardness	6.26	6.27

Low pCO_2

Mineral	Mass, initial, g	Mass at 5000 years, g	Density, g cm^{-3}	Hardness
Quartz	7900	7900	2.62	7
Calcite	700	1000	2.71	3
Dolomite	1100	731	2.84	3.75
Kaolinite	100	100	2.6	1.75
Albite	100	100	2.62	7
Muscovite	100	100	2.82	2.25
Gypsum	0	69.0	2.3	2
Nontronite	0	0.005	2.3	1.75

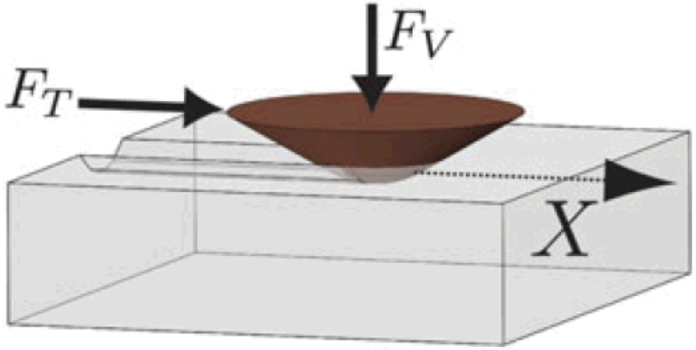
	Initial	After 5,000 years
Rock mass, g	10,000	10,000
Average density	2.65	2.64
Average hardness	6.26	6.23

CO_2-related alteration and micro-scratch test

1

1. Autoclave experiment: quickly alter the sample but with limited penetration depth
2. Micro-scratch test can probe the reacted skin
3. Mechanical properties are obtained from load-displacement curve

2



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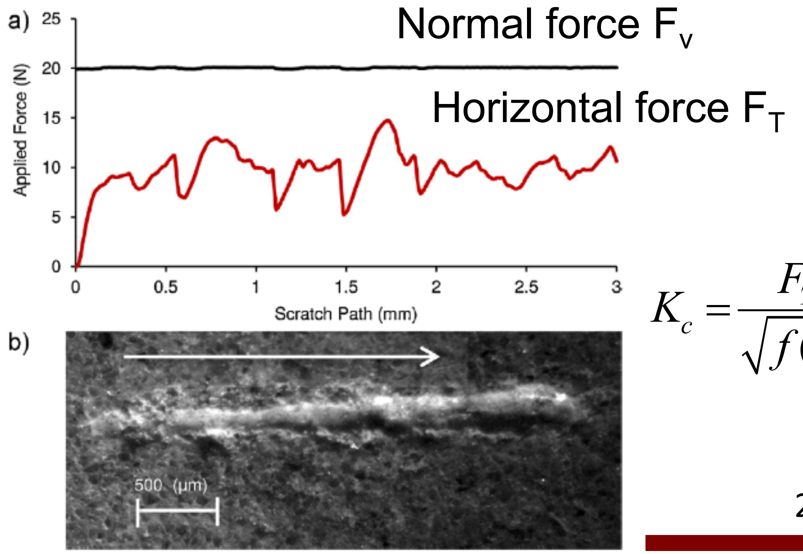


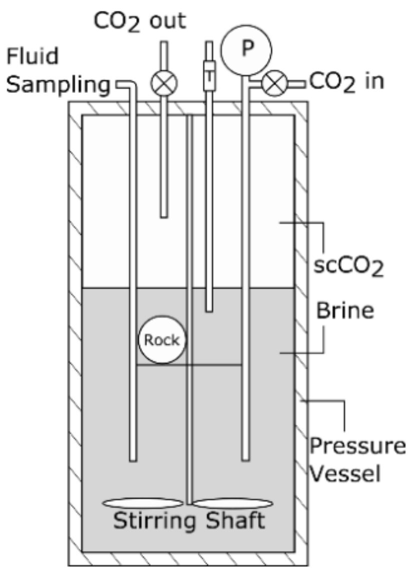
$$K_c = \frac{F_T}{\sqrt{f(d)}}$$

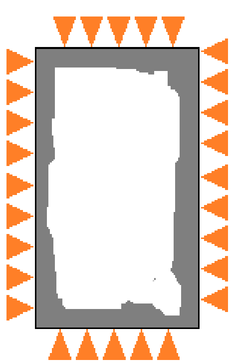
Akono et al., 2011

Sun et al., 2016

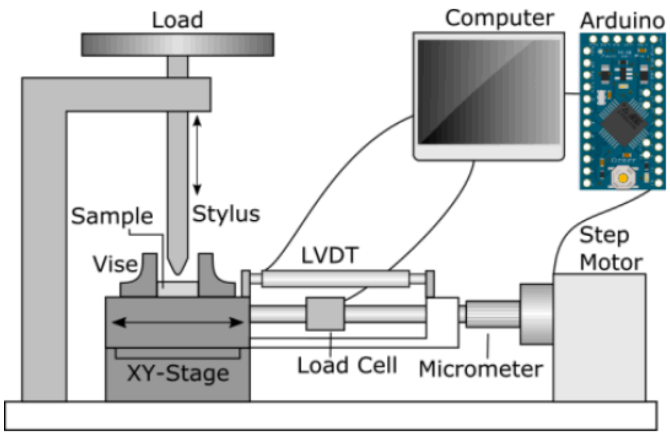
Scratch Testing

Autoclave reactor:

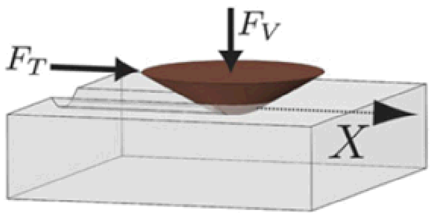




Scratch test:



$$K_c = \frac{F_T}{\sqrt{f(d)}}$$



Akono et al., 2011