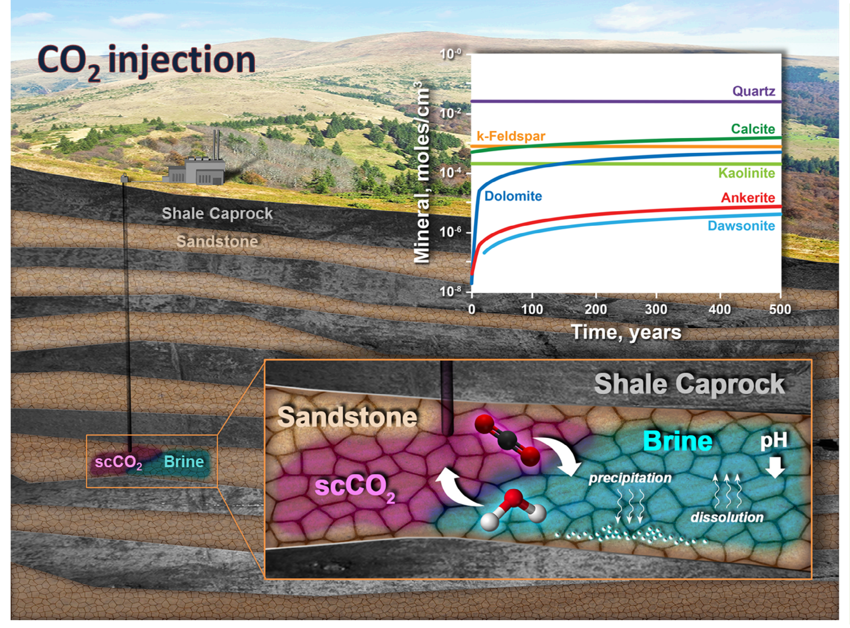
SAND2017-0540D

Shale-brine-CO_2 Interactions and the Long-term Stability of Shale Caprock

A. Ilgen[1], M. Aman[2], J. Feldman[1], J. Kruichak[1], N. Espinoza[2], T. Dewers[1], and C. Choens[1]

[1] Sandia National Laboratories, [2]University of Texas at Austin

Coupled chemo-mechanical processes in shale caprock

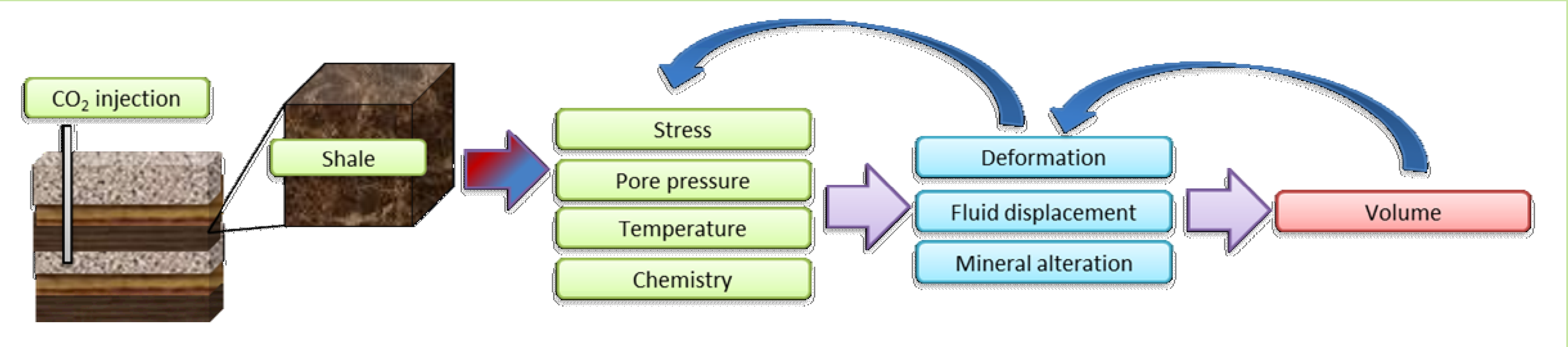


Schematic for geological carbon storage (adopted from [13])

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 (mudrock) 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]

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



Coupled physico-chemical processes in response to the CO_2 injection

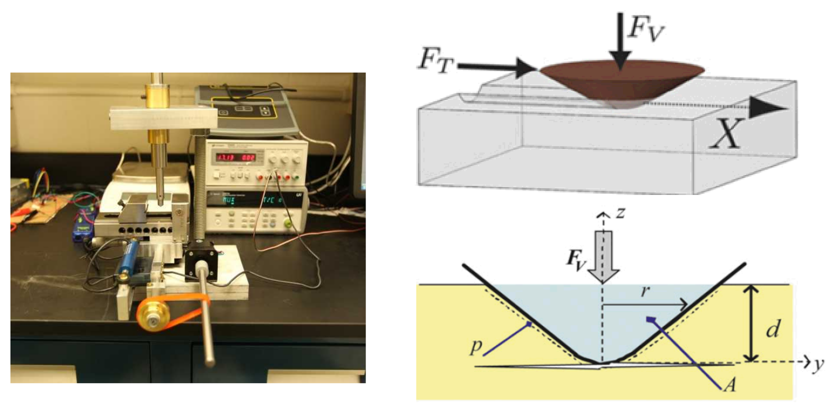
Methods

Laboratory experiments: alteration of shale samples at conditions typical of GCS to understand time-dependent geochemical reactions.
Aqueous sample analysis: ion chromatography (IC), and inductively coupled plasma mass spectrometry (ICP-MS).
Solid sample analysis: X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, X-ray computed tomography (CT)
Geochemical modeling: Geochemists Workbench.[14]
Scratch testing: to measure resistance of surface deformation induced by the application of vertically loaded stylus. [15,16]

Stirred reactor pressurized with CO_2

pCO_2 = 2500 psi (high pCO_2), and 100 psi (low pCO_2)

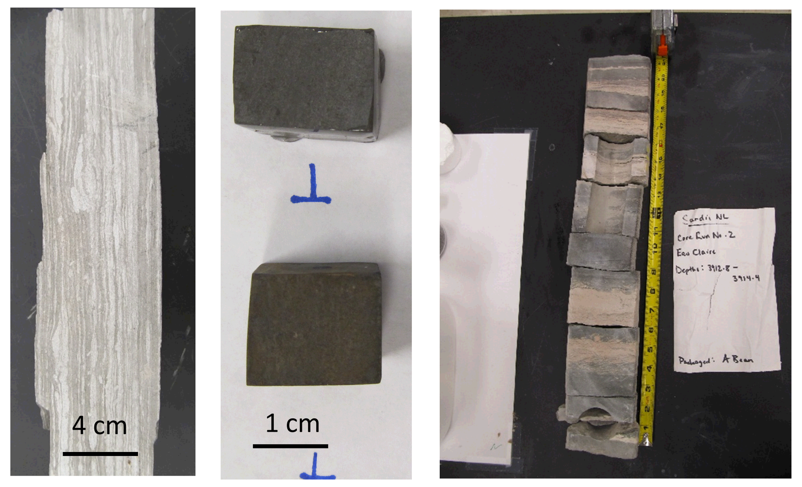
Fracture Toughness: Scratch Test



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

Natural shale samples

Mancos | Woodford | Eau Claire



Synthetic brine

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

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

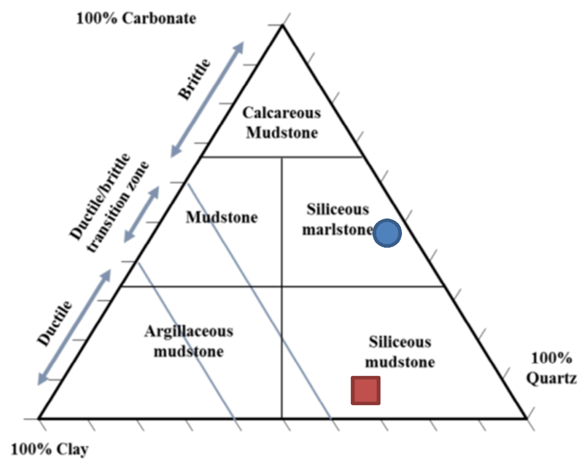
* Developed based on the dataset from "Natural Contamination from the Mancos Shale" Report, US DOE, ESL–RPT–2011–01.
* *Developed based on U.S. Geological Survey National Produced Waters Geochemical Database v2.1, Woodford shale

Shale mineralogy

Mancos
- Quartz 55.1 wt.%
- Calcite 27.2 wt.%
- Dolomite 17.7 wt.%
- Kaolinite
- Pyrite
- Albite
- Biotite

Woodford
- Quartz 61.9 wt.%
- Illite 32.5 wt.%
- Chlorite 4.4 wt.%
- Calcite 1.3 wt.%
- Biotite
- Hematite

Eau Claire
- Quartz
- Orthoclase
- Illite
- Clinochlore



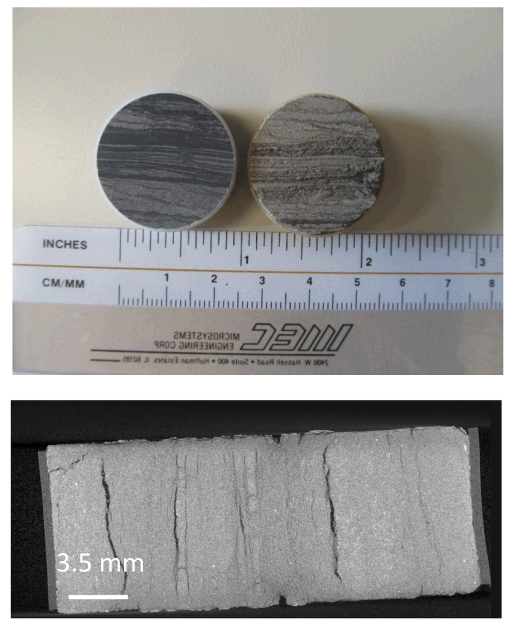
Mineralogical classification of mudstones [17,18]

References

[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
[13] Ilgen and Cygan, 2016
[14] Bethke, 2008
[15] ASTM G171
[16] Akono and Ulm, 2011
[17] Grigg, 2015
[18] Ulmer-Scholle et al, 2014
[19] Liu et al., 2012

Alteration of Mancos shale by CO_2-brine mixtures

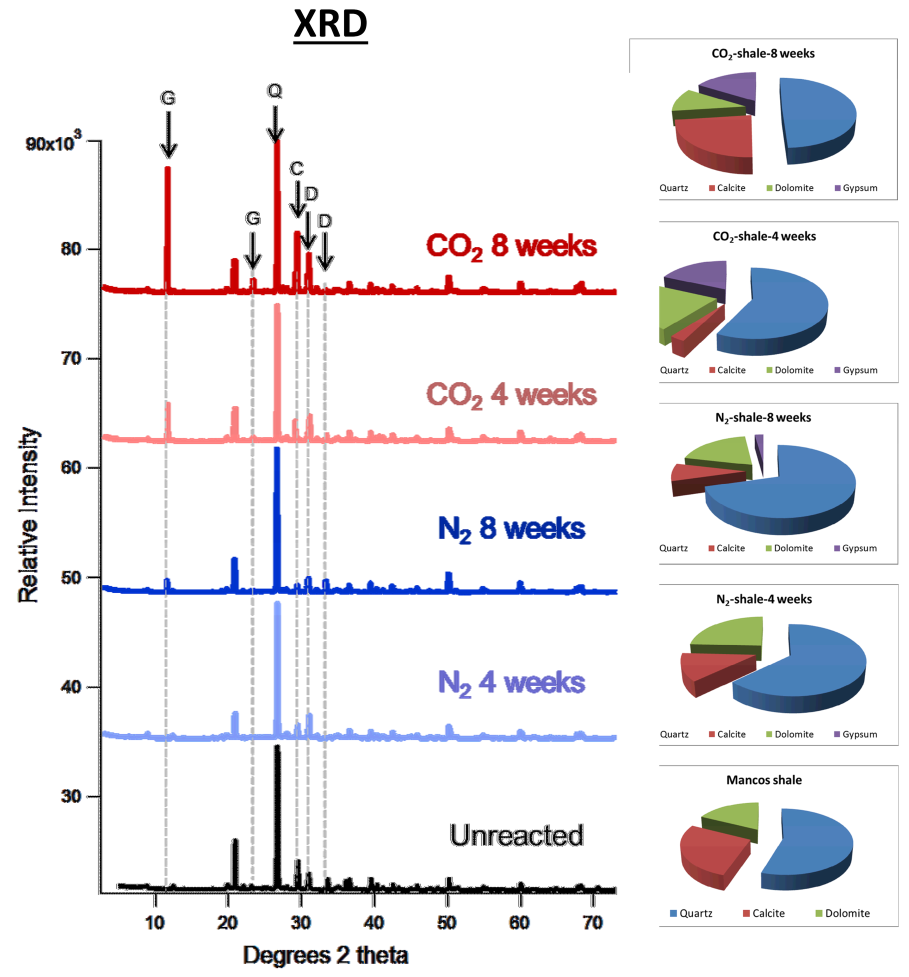
Aqueous chemistry observations (low pCO_2): pH is buffered by the dissolution of CO_2 into brine, and dissolution of carbonates (calcite and dolomite). Positive Na-K correlation indicates no cation exchange (consistent with the absence of swelling clay minerals). Ca and Sr are more soluble in pCO_2 vs. control reactors. Fe solubility is low, slightly more soluble in high-pCO_2-pressurized reactor. Al is below the detection limit.
Mineralogy: Dedolomitization – dolomite is replaced by calcite over the 2-month alteration reaction. Geochemical modeling also predicts alteration of muscovite to gibbsite.



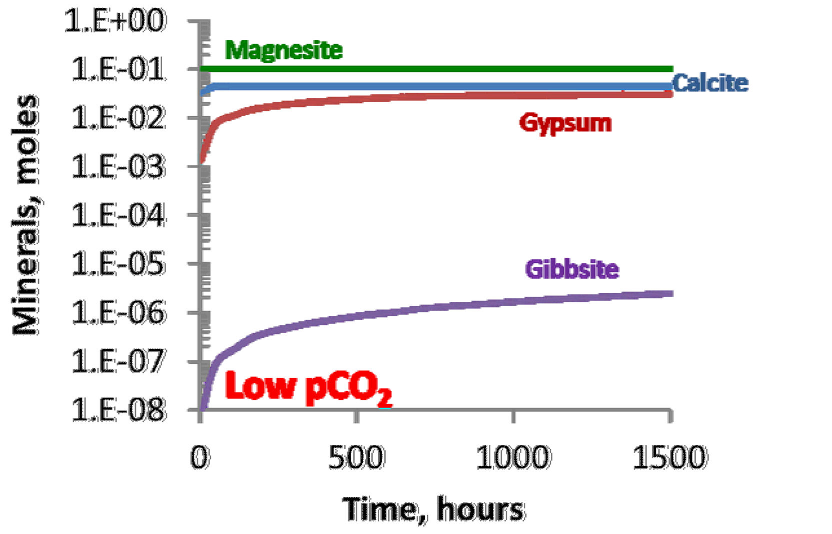
Altered depth ~1-1.5 mm

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

XRD



Geochemical modeling



Main alteration reactions

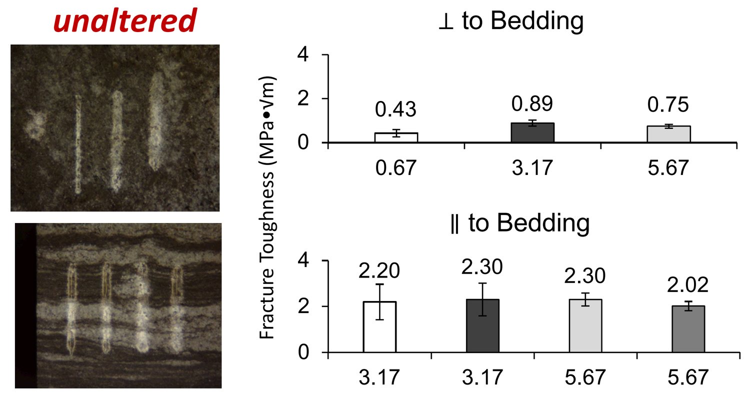
$CaCO_{3(s)}$ (calcite) + $2H^+$ → Ca^{2+} + H_2CO_3

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

→ Mg^{2+} + H_2CO_3 → $MgCO_{3(s)}$ (magnesite) + $2H^+$
→ Ca^{2+} + H_2CO_3 → $CaCO_{3(s)}$ (calcite) + $2H^+$
→ Ca^{2+} + SO_4^{2-} → $CaSO_{4(s)}$ (gypsum) + $2H^+$

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

Scratch testing

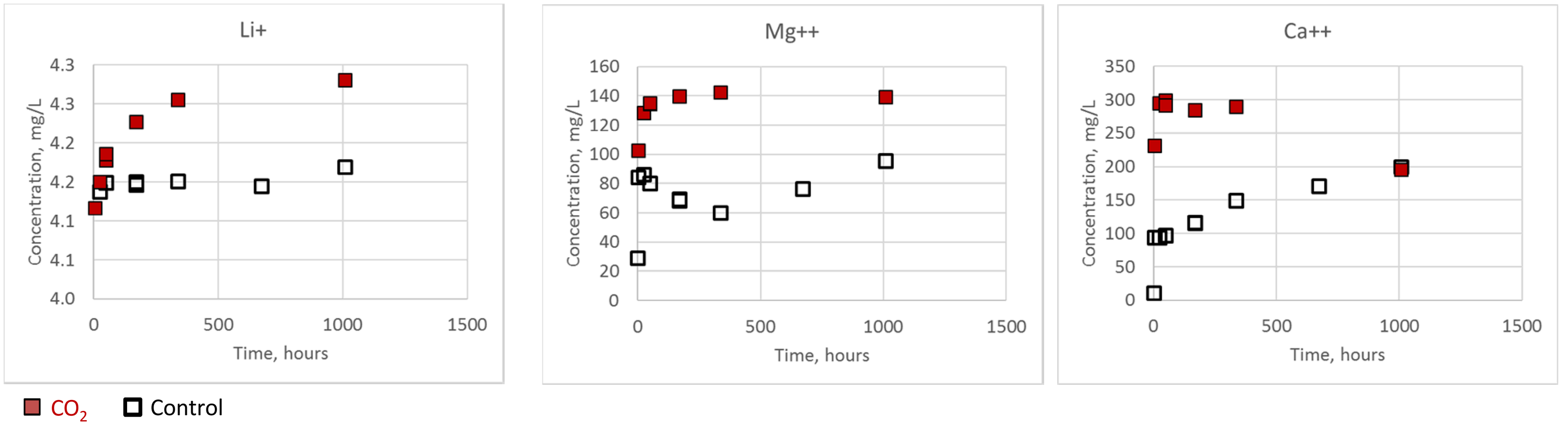


Summary: Alteration by CO_2-brine mixture maybe causing net decrease in density and hardness, which may result in shale weakening.

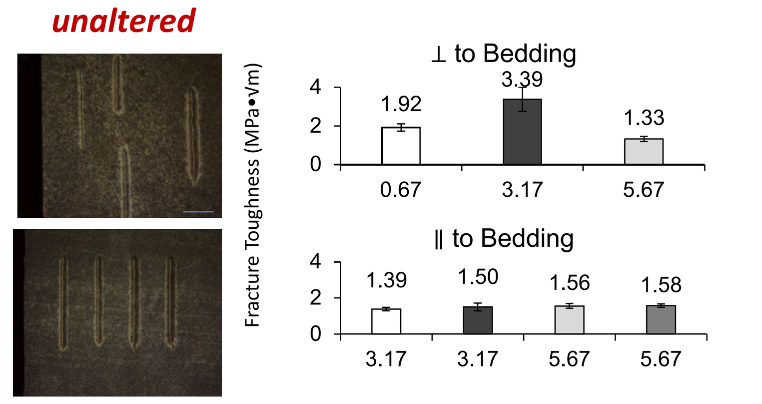
Alteration of Woodford shale by CO_2-brine mixtures

Aqueous chemistry observations (high pCO_2): Li, Mg, Ca, and sulfate are released from Woodford shale. Mg, Ca and Li are more soluble in high pCO_2 vs. control reactors.
Mineralogy: trace amount of calcite and silicate cement dissolution.

Aqueous chemistry



Scratch testing



Summary: Mineral alteration is more pronounced in CO_2-containing reactors compare to the controls. Dissolution of silicate and carbonate cement may be weakening Woodford shale.

Acknowledgements
Mark Rodriguez and James Griego, Sandia National Labs, performed X-ray Diffraction analysis.

U.S. DEPARTMENT OF ENERGY
National Nuclear Security Administration

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-mission 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.