CFSES CENTER FOR FRONTIERS OF SUBSURFACE ENERGY SECURITY

U.S. DEPARTMENT OF ENERGY

Micromechanical tests and geochemical modeling to evaluate evolution of rock alteration by CO2-water mixtures

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SAND2015-6783C

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Introduction

The injection of CO_2 underground may shift the chemical interaction of minerals and the pore fluid far from equilibrium. Field and laboratory experiments have shown that this shift will situationally facilitate mineral dissolution and reprecipitation of load carrying minerals and affect the long term mechanical stability of the host formation [Lu et al., 2012; Carroll et al., 2011; Carroll et al., 2013; Major et al., 2014].

Chemo-mechanical coupling

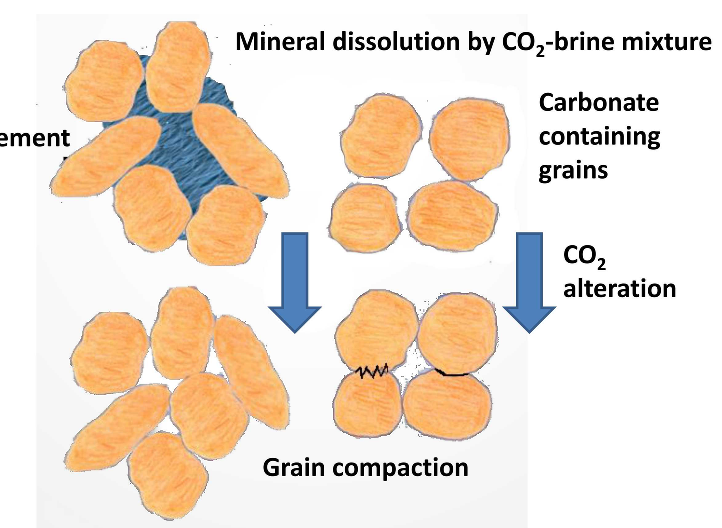
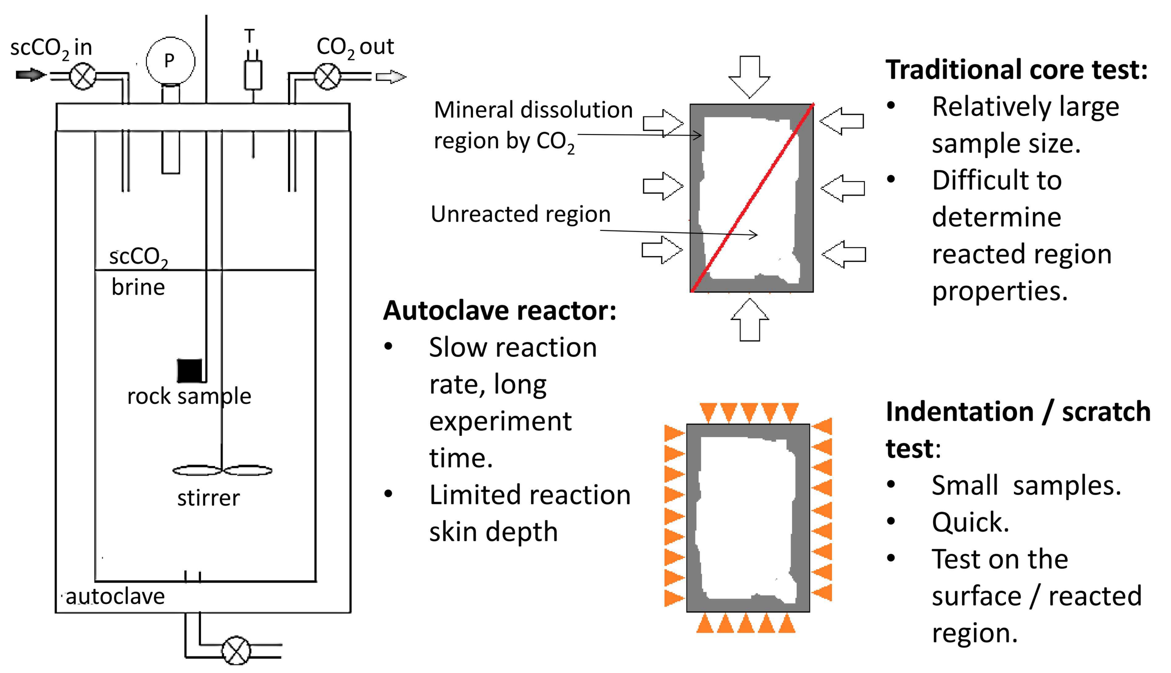


Fig.1. Schematic of how mineral dissolution by CO_2-brine mixture could cause formation compaction. [Railsback, 2006]

Degradation of mechanical properties can facilitate reservoir compaction caprock bending above dissolving reservoir zones [Kim & Santamarina, 2014].

Micromechanical tests are well suited to identifying properties of rock samples altered through easy-to-perform autoclave reactions that result in a limited skin depth of chemical alteration.



Traditional core test:
- Relatively large sample size.
- Difficult to determine reacted region properties.

Autoclave reactor:
- Slow reaction rate, long experiment time.
- Limited reaction skin depth

Indentation / scratch test:
- Small samples.
- Quick.
- Test on the surface / reacted region.

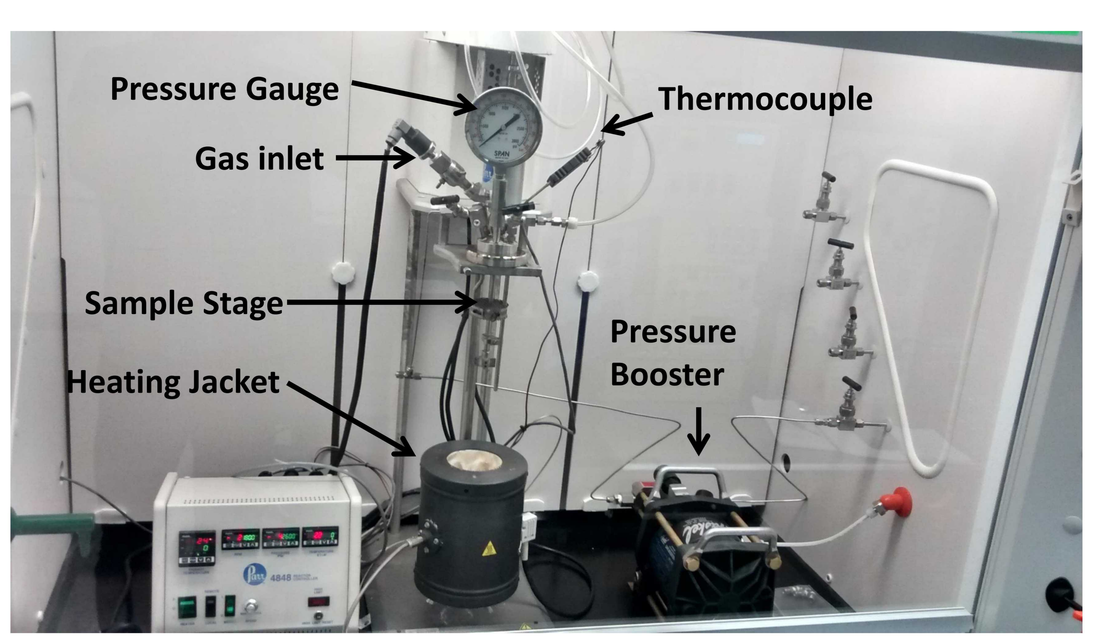


Fig.2. (Left) Schematics of a typical autoclave reactor for CO_2-brine on rock reaction. (Right) Comparison between traditional core-scale test and indentation & scratch tests on CO_2-reacted rock samples. (Below) Labeled picture of experimental setup

Objectives

- Quantify variation of elastic and strength mechanical parameters of silicic and carbonate reservoir rocks exposed to CO_2-water mixtures.
- Identify time scales associated to chemo-mechanical couplings through experimental results and geochemical modeling.
- Determine constitutive parameters from time-dependent experimental data to couple with geomechanical reservoir simulation.
- Validate micromechanical tests as screening tools to evaluate the alteration of mechanical properties of reservoir rocks under geological CO_2 storage conditions.

Sample Preparation

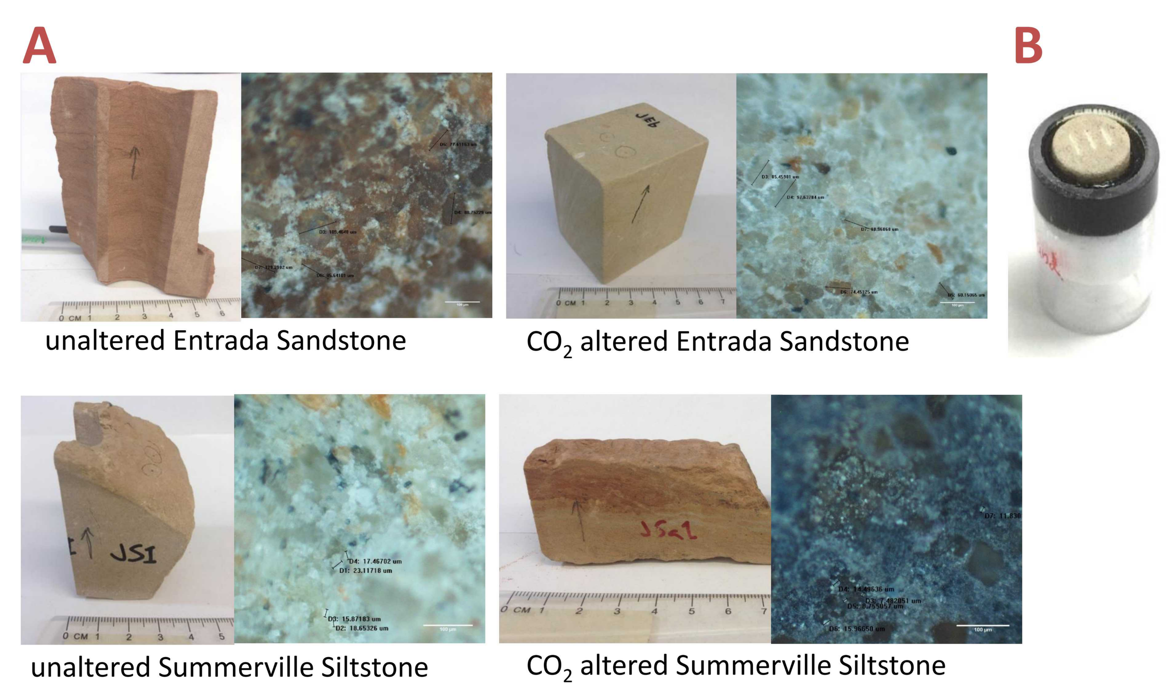
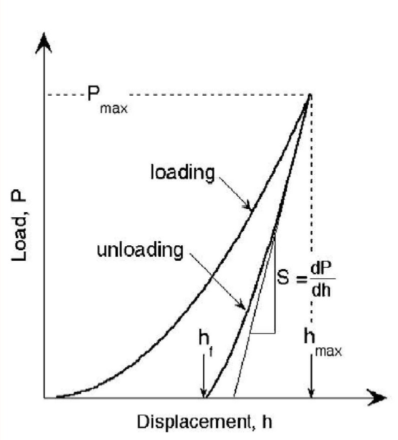


Fig.5. (A) Rock samples taken from Crystal Geyser site, Utah. (B) A polished, epoxy-casted rock specimen with scratches.

Methods – Micro Indentation Test

A pyramid-shaped Berkovich indenter penetrates the specimen, inducing plastic and elastic deformation, from which mechanical properties of the material can be determined.



Indentation Hardness (H):

$$H = \frac{P_{max}}{A_c},\ [\text{GPa}]$$

Elastic Modulus (E):

$$E_r = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_c}}$$

$$\frac{1}{E_r} = \frac{1-\upsilon^2}{E} + \frac{1-\upsilon_i^2}{E_i}$$

Variables:
- P_{max}: Maximum applied load
- A_c: Contact area
- E_r: Reduced elastic modulus
- E_i: Indenter elastic modulus
- ν_i: Indenter Poisson's ratio
- S: Elastic unloading stiffness

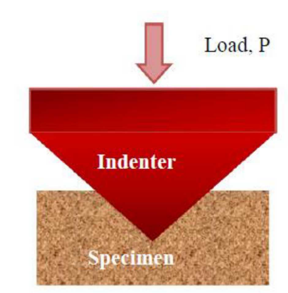


Fig.3. (Top) Indentation load displacement data showing important parameters. Measurements are taken on the unloading cycle [Oliver and Pharr 2004]. (Right) Diagram of penetrating indentation stylus.

Results – Micro Indentation Test

To facilitate brevity and clarity, only representative images of Entrada sandstone test results are shown. See handout for complete results.

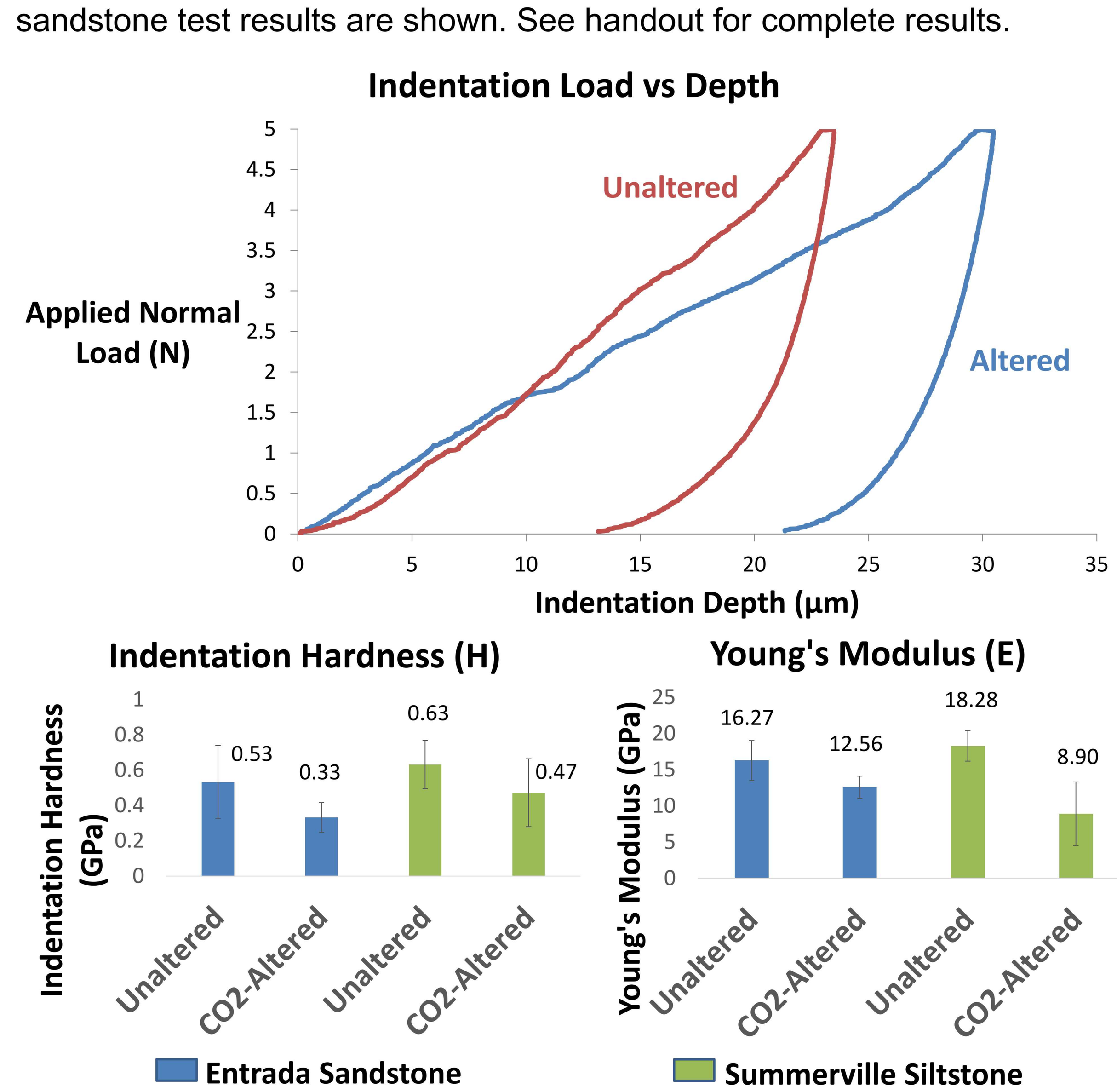
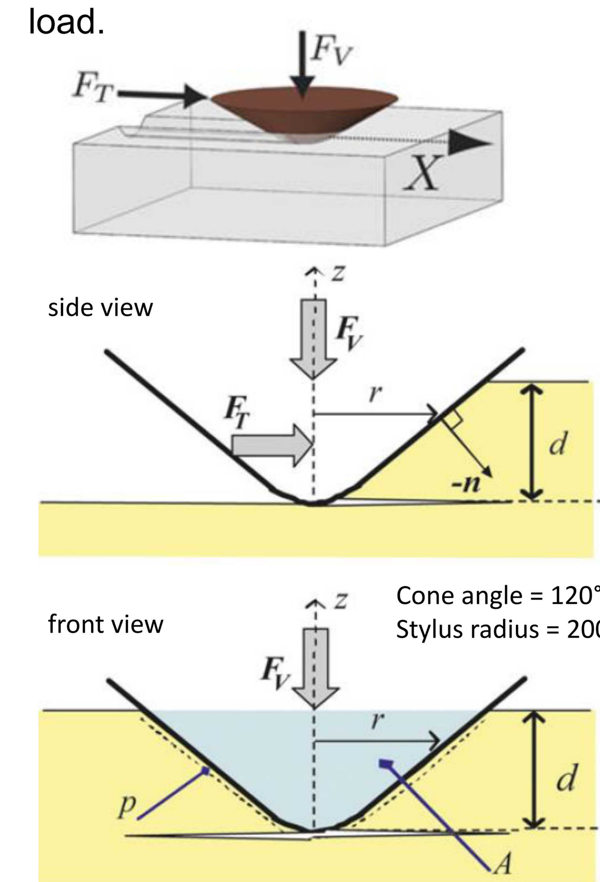


Fig.7. (Top) Indentation normal load versus depth for a single representative pair of unaltered and geologically CO_2-altered Entrada sandstone indentations. Average indentation hardness (bottom left) and mean Young's modulus (bottom right) calculated for both Entrada sandstone and Summerville siltstone, CO_2-unaltered and altered, respectively. Error bars represent 95% confidence intervals. 5 indentations were performed for each type of sample.

Methods - Micro Scratch Test

Scratches are made on the sample with a sphero-conical stylus which is drawn at a constant speed across the sample, under a constant normal load.



Fracture Toughness (K_c):

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

Scratch Hardness ($H_{scratch}$):

$$H_{scratch} = \frac{kF_V}{w^2},\ [\text{GPa}]$$

Variables:
- F_T: Horizontal force
- F_V: Vertical force (constant)
- p: Stylus perimeter
- A : Projected horizontal load bearing contact area
- k: Geometric constant
- w: Scratch width

Fig.4. (Top) Diagram of scratch test showing translation direction. (Middle) Side view and (Bottom) front view of loaded axisymmetric stylus with relevant parameters. [Akono et al., 2012, ASTM G171]

Results - Micro Scratch Test

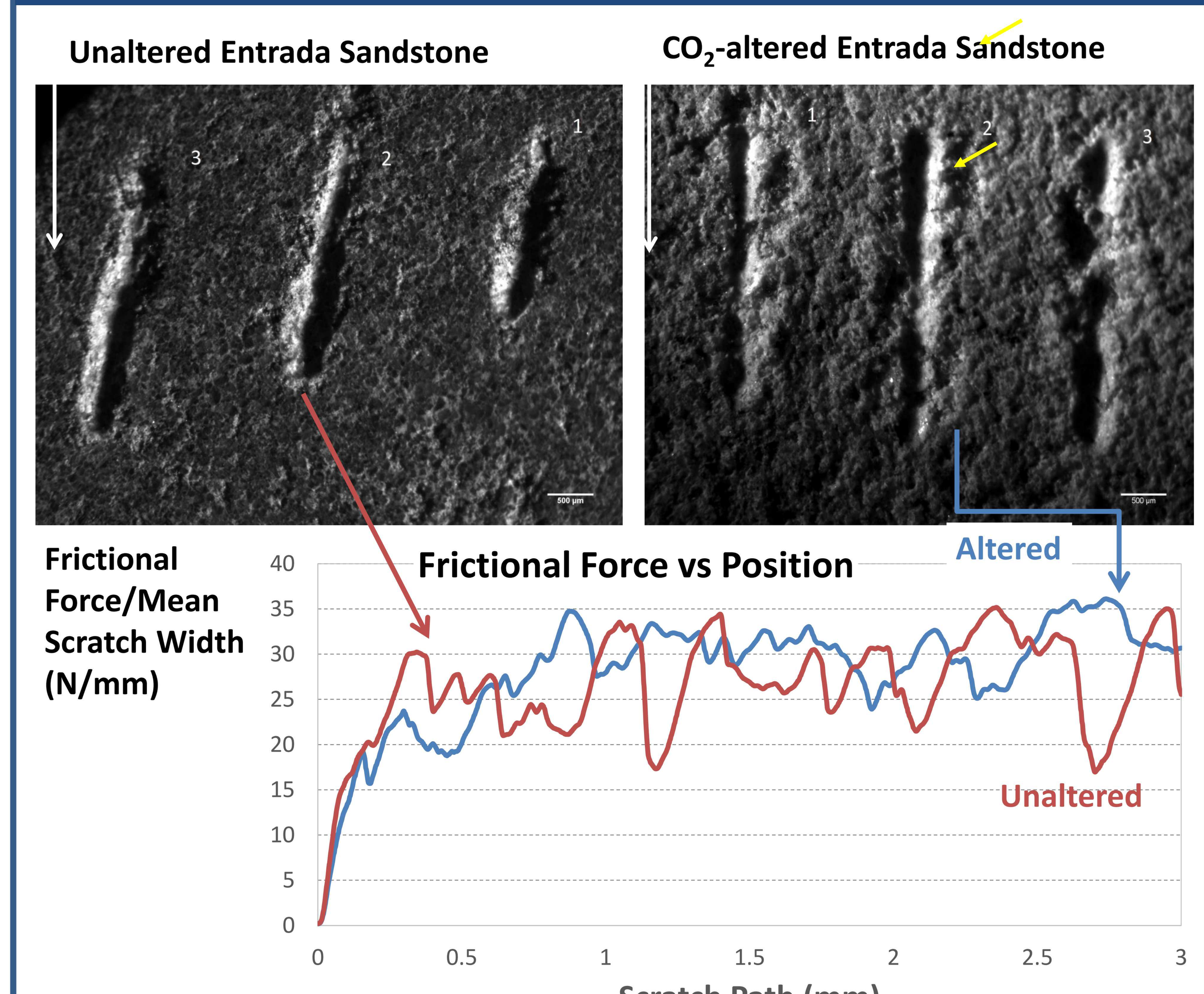


Fig.6. (Top) Stereoscopic images of scratches. White arrows indicate direction of travel. Blueired arrows indicate scratches plots correspond to. Yellow arrows indicate potentially damaged areas not included in width measurements. (Bottom) Frictional force versus scratch position. Normal force was applied at constant 20 N.

The fracture toughness (Mode II) values from scratching are systematically higher than values obtained by Major et al., 2014 using a double torsion test (Mode I), though both result sets show decreasing trends.

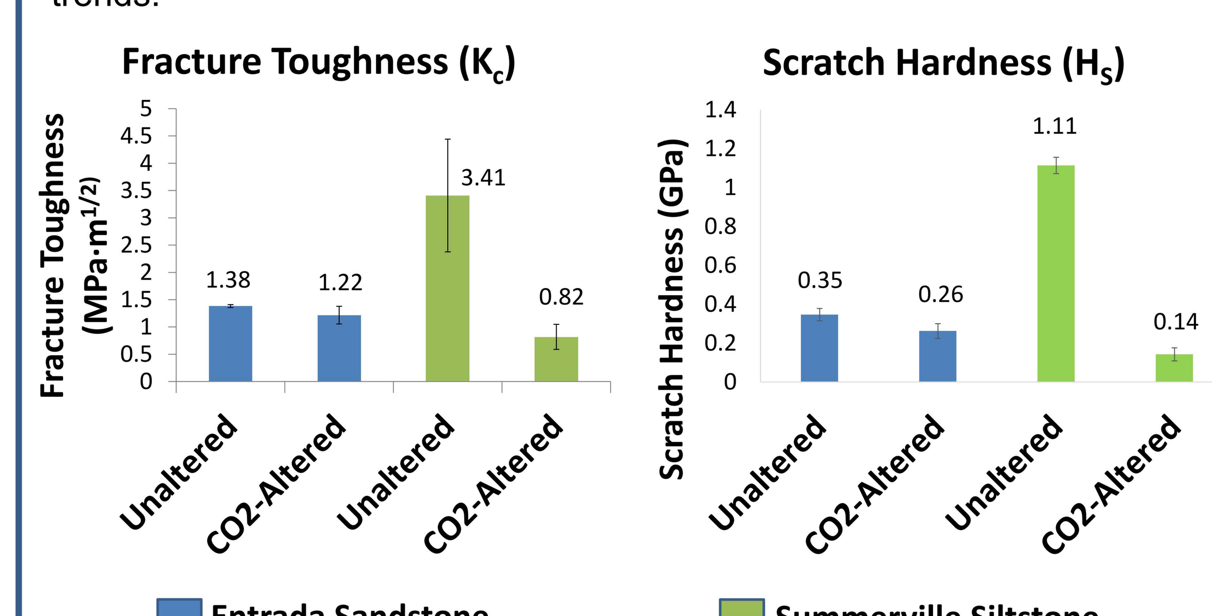


Fig.7. Average fracture toughness (left) and mean scratch hardness (right) calculated for both Entrada sandstone and Summerville siltstone, CO_2-unaltered and altered, respectively. Error bars represent 95% confidence intervals.

Results – Geochemical Modeling

The Geochemist's Work Bench (GWB) Path of Reaction Modeling (Bethke, 1998), is used to predict the changes in mineralogical composition in Entrada sandstone during its alteration by CO_2-charged brine.

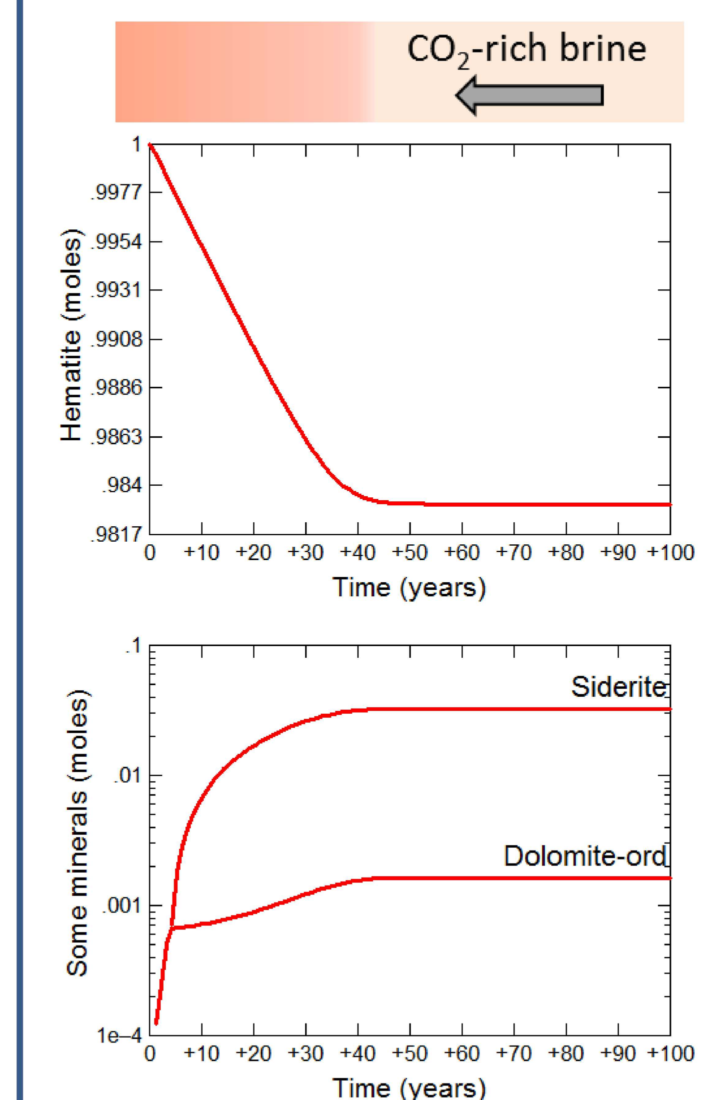


Fig.8. Numerical model: alteration of Entrada sandstone by CO_2-charged brine. Hematite dissolution (top), and siderite and dolomite precipitation (bottom) are predicted.

Table 1. Input for the path of reaction models: initial composition of Entrada sandstone brine, and amounts of reacting carbon dioxide and methane.

Input		
pH	8.1	
Eh	0	
Na^+	24200	mg/l
K^+	1	mg/l
Mg^{++}	315	mg/l
Ca^{++}	1455	mg/l
Fe^{++}	1	mg/l
Cl^-	37950	mg/l
HCO_3^-	762.5	mg/l
SO_4^{--}	3250	mg/l
$SiO_2(aq)$	Equilibrium with quartz	
Reactants		
30 mmol of $CO_2(aq)$		
5 mmol of $CH_4(aq)$		

Table 2. Input for the path of reaction models: mineral assemblage, reactive surface areas, and kinetic rate constants.

Mineral	Specific surface area, cm^2/g	Kinetic rate constant log (mol/cm^2 sec)
Quartz	10	-16
K-feldspar	10	-15
Hematite	10	-14
Calcite	10	-8

The initial brine composition is based on the compilation of ground-water chemistry for the Green River Formation (Wanty et al., 1991). This brine was reacted with CO_2 and CH_4, and minerals quartz, K-feldspar, calcite, and hematite. The concentrations of CO_2 and CH_4 in the reactive fluid are chosen based on Wigley et al., 2012.

Conclusions & Future Work

- Long term exposure of Crystal Geyser rocks to reactive CO_2-water mixtures resulted in mechanical degradation as shown by significant decreases in hardness and fracture toughness.
- We will assess rock-water-CO_2 reaction kinetics and rock mechanical degradation through scratch and indentation experiments and reaction modeling on rocks altered via autoclave over laboratory time scales.
- Fracture property trends determined from scratch tests validate previous mechanical testing performed on same source rock samples.
- Microscratch tests may have further applications in geomaterials across the meso- and microscale, e.g. capturing down well mechanical property variation.

Acknowledgements

This research is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The Center for Frontiers of Subsurface Energy (CFSES) is a DOE Energy Frontier Research Center, under Contract No. 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.

References

Akono, A., Randall, N., & Ulm, F. (2012). Experimental determination of the fracture toughness via microscratch tests: Application to polymers, ceramics, and metals. *Journal of Materials Research, 27*(2), 485-493.
Bethke C. (1998) The Geochemist's Workbench 8.0. University of Illinois at Urbana-Champaign, IL.
Carroll, S., Mcnab, W., & Torres, S. (2011). Experimental Study of Cement - Sandstone/Shale - Brine - CO_2 Interactions. *Geochemical Transactions, 2011*(12), 9-9.
Carroll, S., Hao, Y., Smith, M., Sholokhova, Y. (2013), Development of scaling parameters to describe CO_2-carbonate-rock interactions for the Marly Dolostone and Vuggy Limestone, *International Journal of Greenhouse Gas Control, 16*(1), S185-S193.
Kim, S., & Santamarina, J. C. (2014). CO2 geological storage: hydro-chemo-mechanical analyses and implications. *Greenhouse Gases: Science and Technology*, *4*(4), 528-543.
Lu, J., Kharaka, Y.K., Thordsen, J.J., Horita, J., Karamalidis, A., Griffith, C., Hakala, J.A., Ambats, G., Cole, D.R., Phelps, T.J., Manning, M.A., Cook, P.J., Hovorka, S.D., (2012). CO_2–rock–brine interactions in Lower Tuscaloosa Formation at Cranfield CO_2 sequestration site, Mississippi, U.S.A. *Chemical Geology 291*, 269–277.
Major, J.R., Eichhubl, P., Dewers, T.A., Urquhart, A.S., Olson, J.E., & Holder, J. (2014). The effect of CO_2-related diagenesis on geomechanical failure parameters: Fracture testing of CO_2-altered reservoir and seal rocks from a natural analog at Crystal Geyser, Utah. *American Rock Mechanics Association, 14-7463*.
Oliver, W., & Pharr, G. (2004). Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *Journal of Materials Research, 19*(1), 3-20.
Railsback, B. (2006) Some Fundamentals of Mineralogy and Geochemistry. University of Georgia at Athens, GA.
Santarelli, F., Detienne, J., & Zundel, J. (1991). The use of a simple index test in petroleum rock mechanics. *Rock Mechanics as a Multidisciplinary Science,* 647-655.
Wanty, R. B.; Pitman, J. K.; Fouch, T. D. Ground-water chemistry and diagenetic reactions in Tertiary sandstones of the Green River and Wasatch formations, Uinta Basin, Utah; 1991.
Wigley, M.; Kampman, N.; Dubacq, B.; Bickle, M., Fluid-mineral reactions and trace metal mobilization in an exhumed natural CO2 reservoir, Green River, Utah. Geology 2012, 40, (6), 555-558.

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