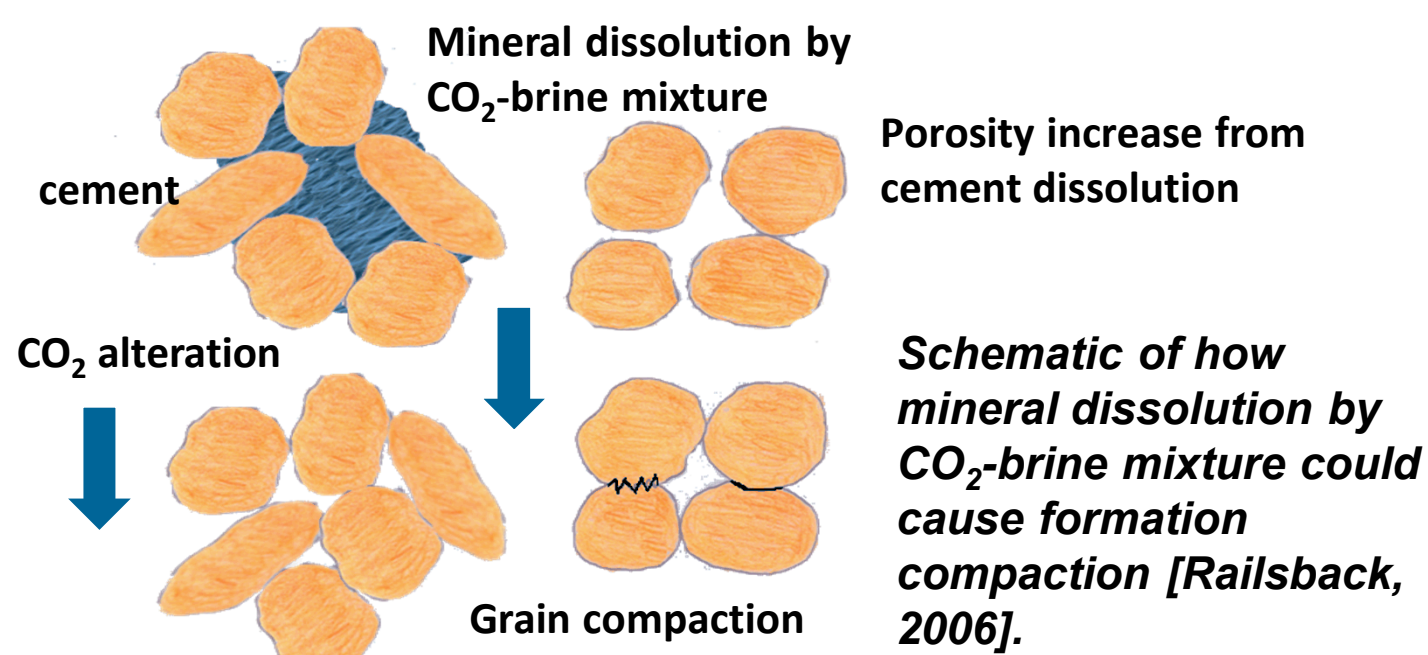


Introduction

Injection of large volumes of CO₂ into geologic formations can help reduce the atmospheric CO₂ concentration and lower the impact of burning fossil fuels. The injection of CO₂ into geologic reservoirs shifts the chemical equilibrium between the mineral assemblage and the pore fluid. Field and laboratory experiments have shown that this shift will situationally facilitate dissolution and re-precipitation of load carrying mineral phases 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].



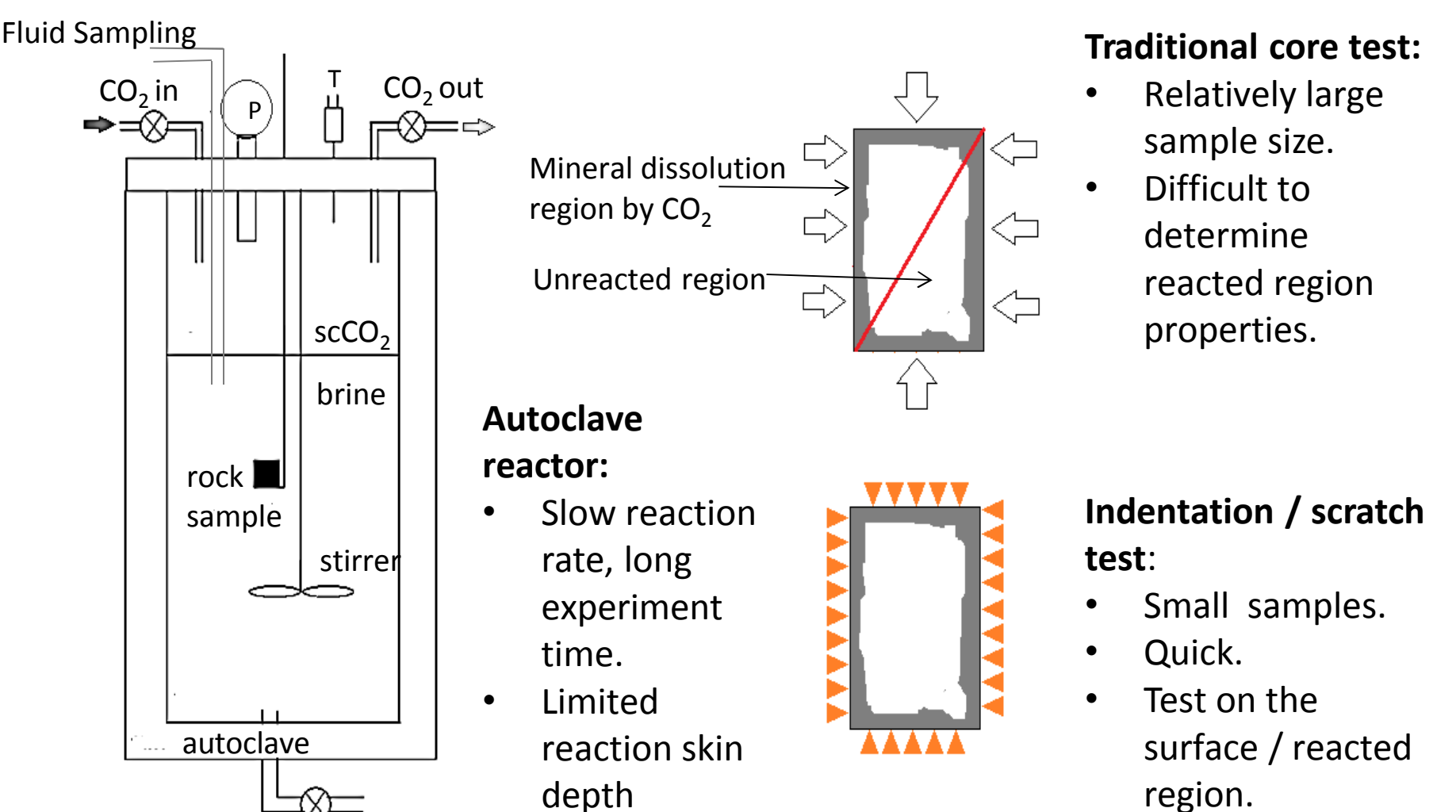
Degradation of mechanical properties can facilitate reservoir compaction and caprock bending above the affected reservoir zones [Kim & Santamarina, 2014].

We show chemical and micro-mechanical testing results on Entrada sandstone and Summerville siltstone (Crystal Geyser, Utah) altered due to exposure to natural CO₂-brine environments as well as on analogous samples altered in controlled laboratory experiments at high pressure, temperature, and in the presence of dissolved CO₂

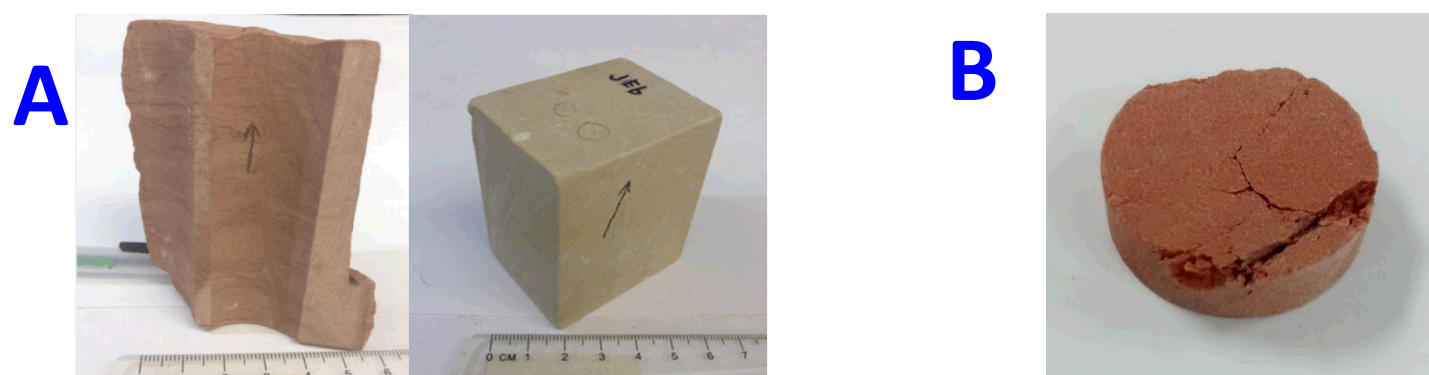
Objectives

- Quantify variation of elastic and strength mechanical parameters of silicic and carbonate reservoir rocks exposed to CO₂-water mixtures to predict emergent chemo-mechanical behavior in CO₂ storage reservoirs
- Identify time scales of the coupled chemical-mechanical reservoir response through experimental evidence
- Determine constitutive parameters from time-dependent experimental data to fit with geochemical modeling

Sample Preparation

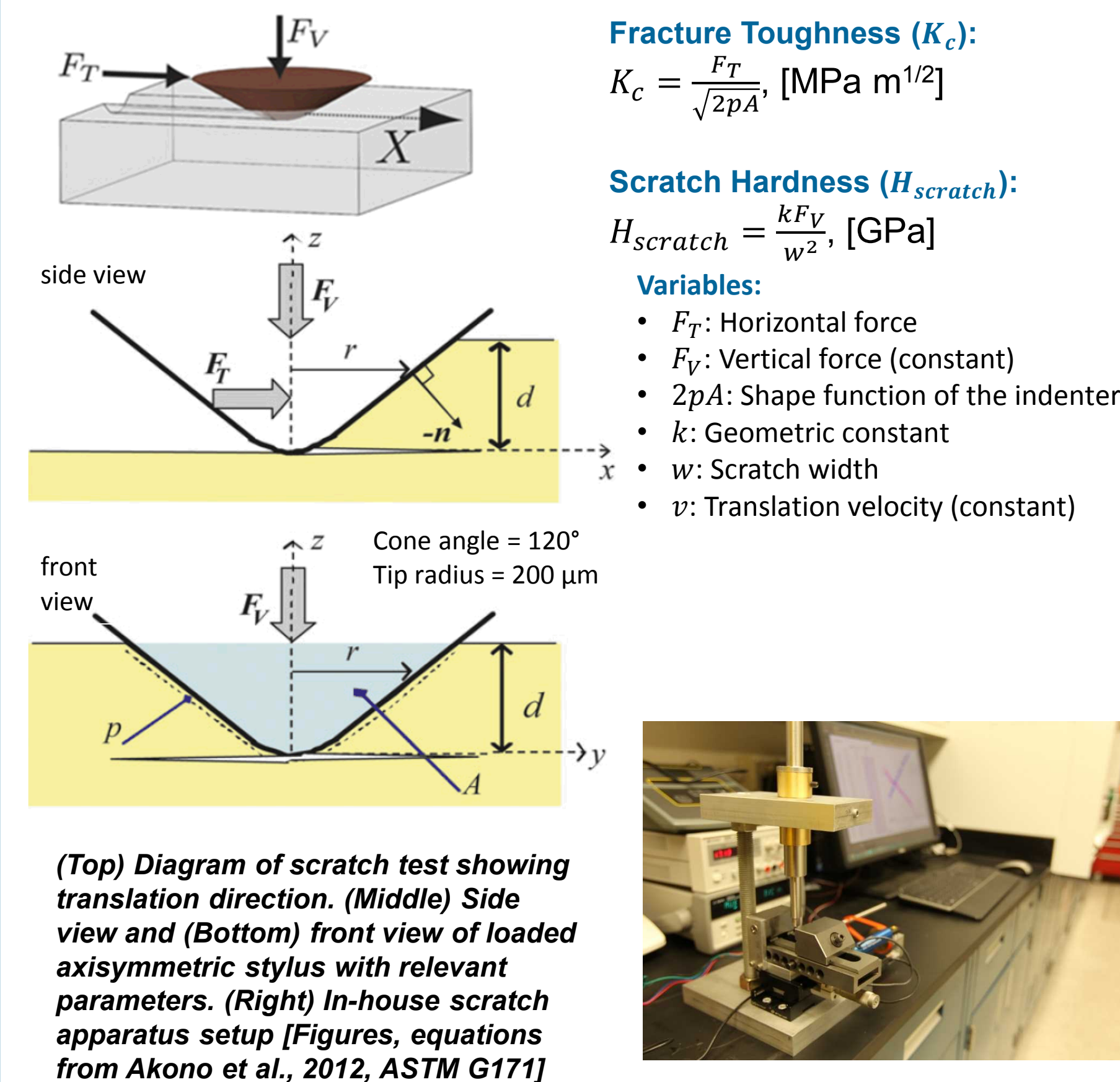


(Left) Schematics of a typical autoclave reactor for CO₂-brine on rock reaction. (Right) Comparison between traditional core-scale test and indentation & scratch tests on CO₂-reacted rock samples. (Below) Labeled picture of experimental setup

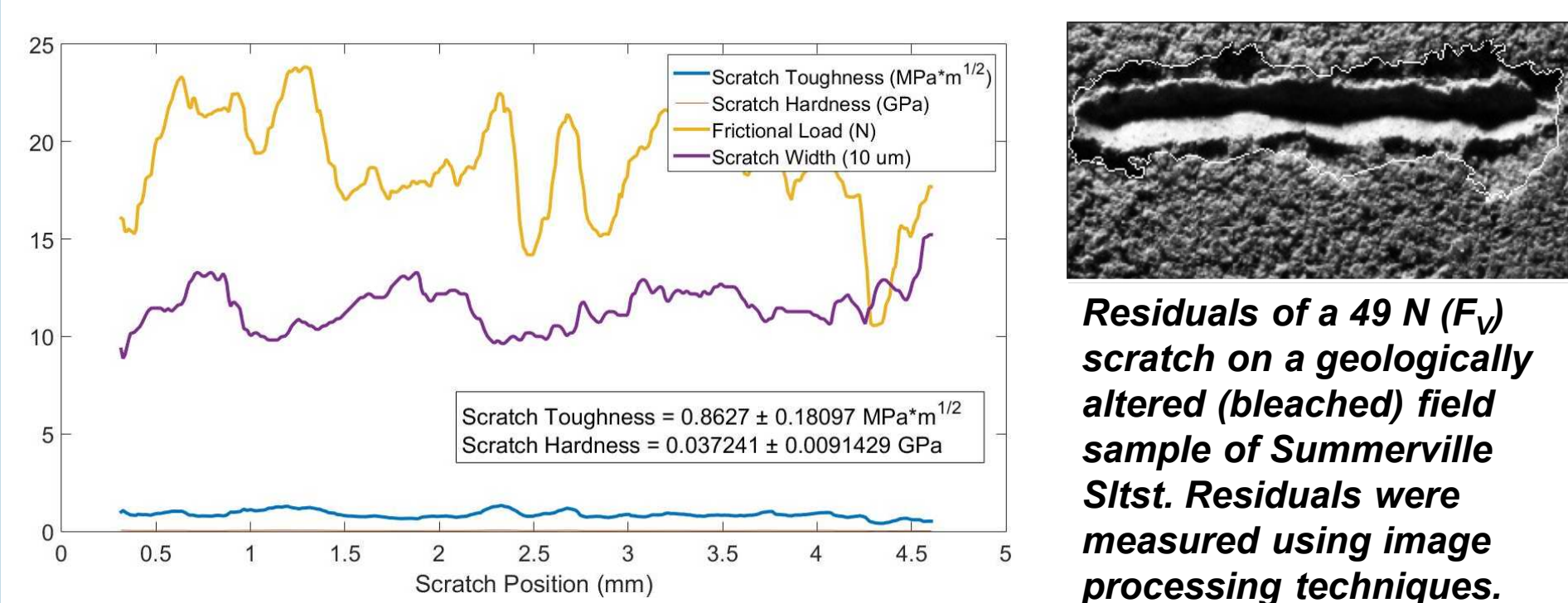


unaltered geologically altered
 Entrada Sandstone
 (A) Rock samples taken from the Crystal Geyser site near Green River, Utah. Samples provided by Jonathan Major from the Bureau of Economic Geology.
 (B) An Entrada Sst sample after alteration in an autoclave with CO₂ and deionized water at 1350 psi and 80C for 2 weeks.

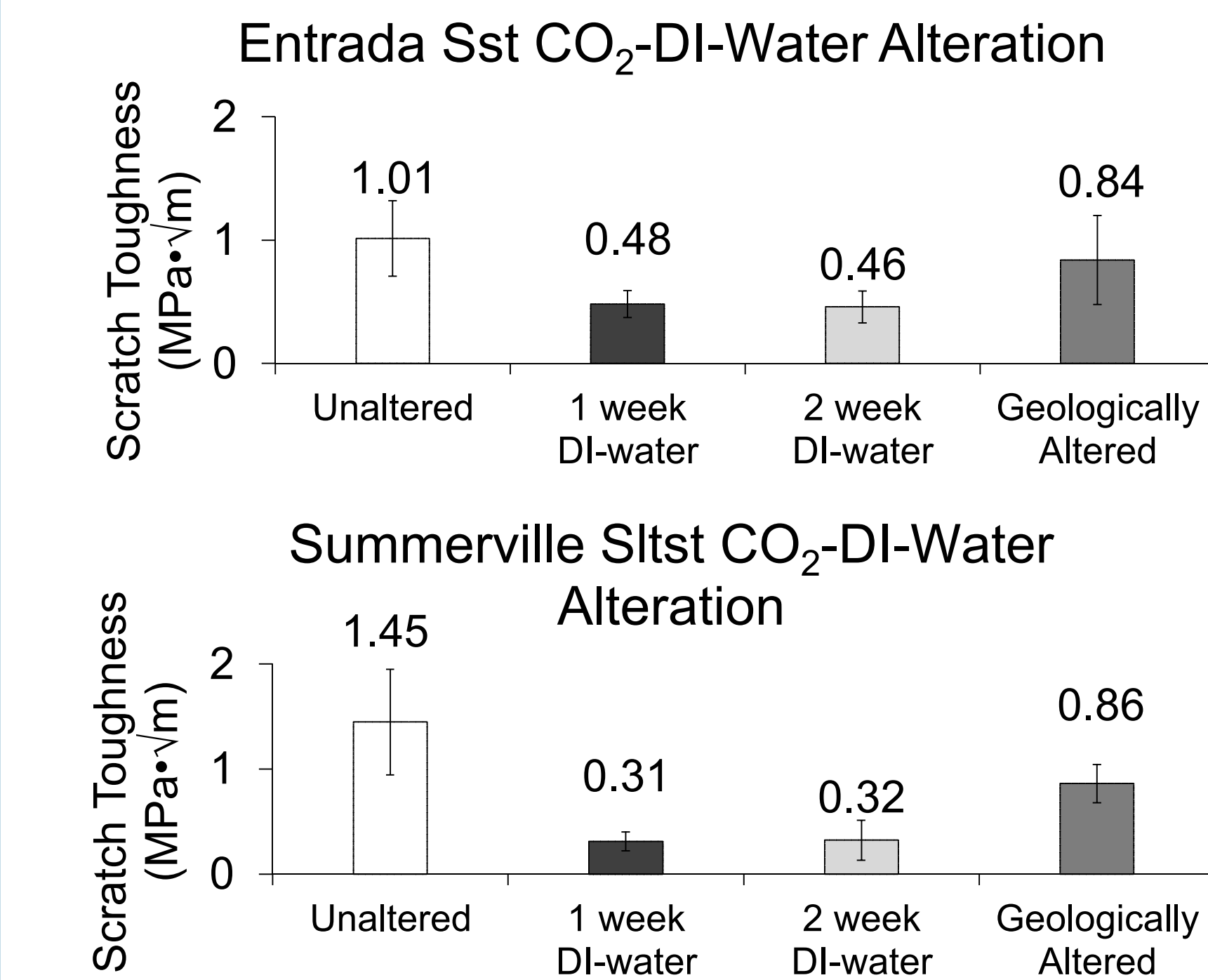
Methods - Micro Scratch Test



Results - Micro Scratch Test

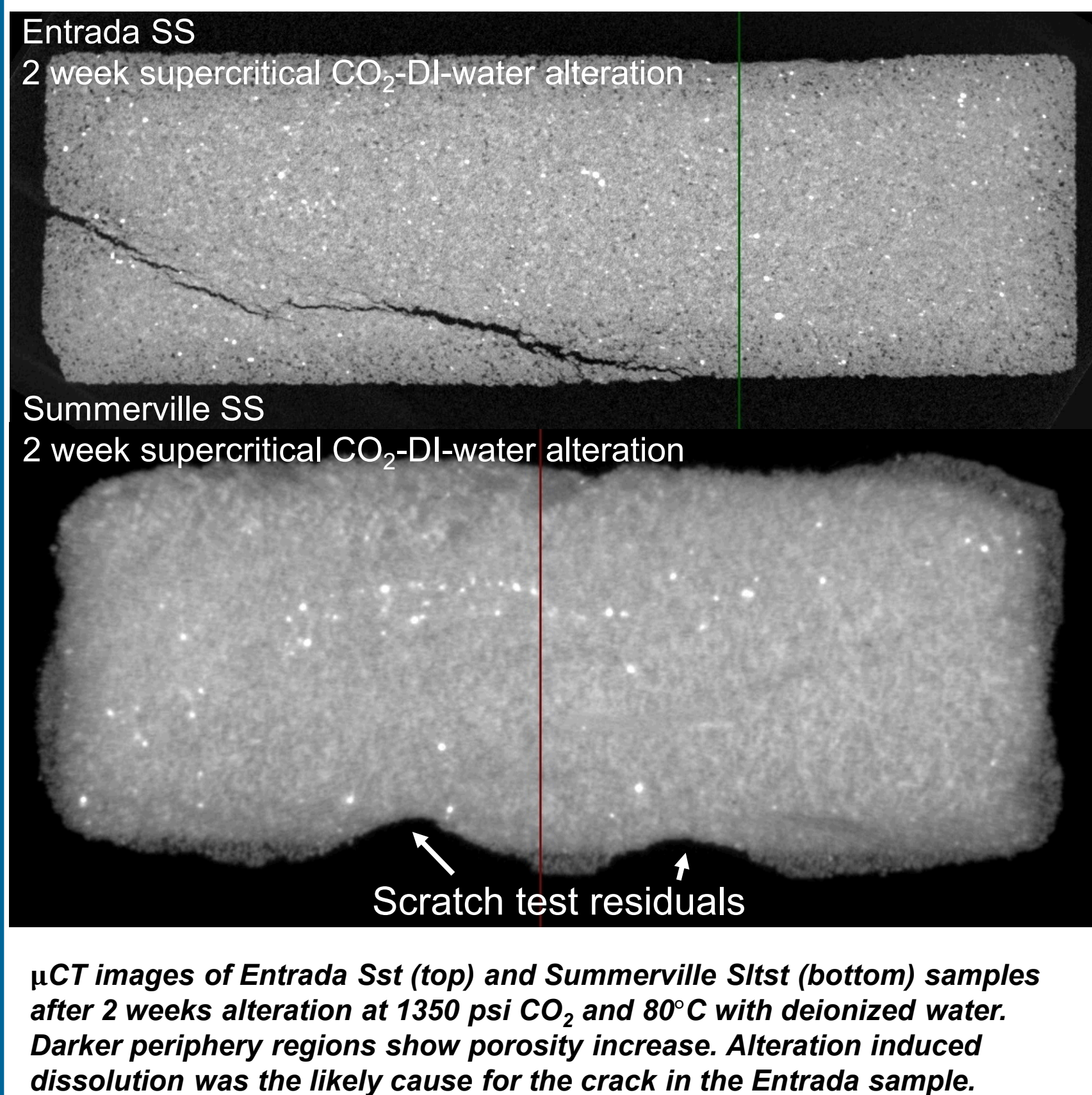


Scratch toughness trends for a bleached sample of Summerville Siltst. Frictional load in yellow; scratch width in purple; scratch toughness in blue.



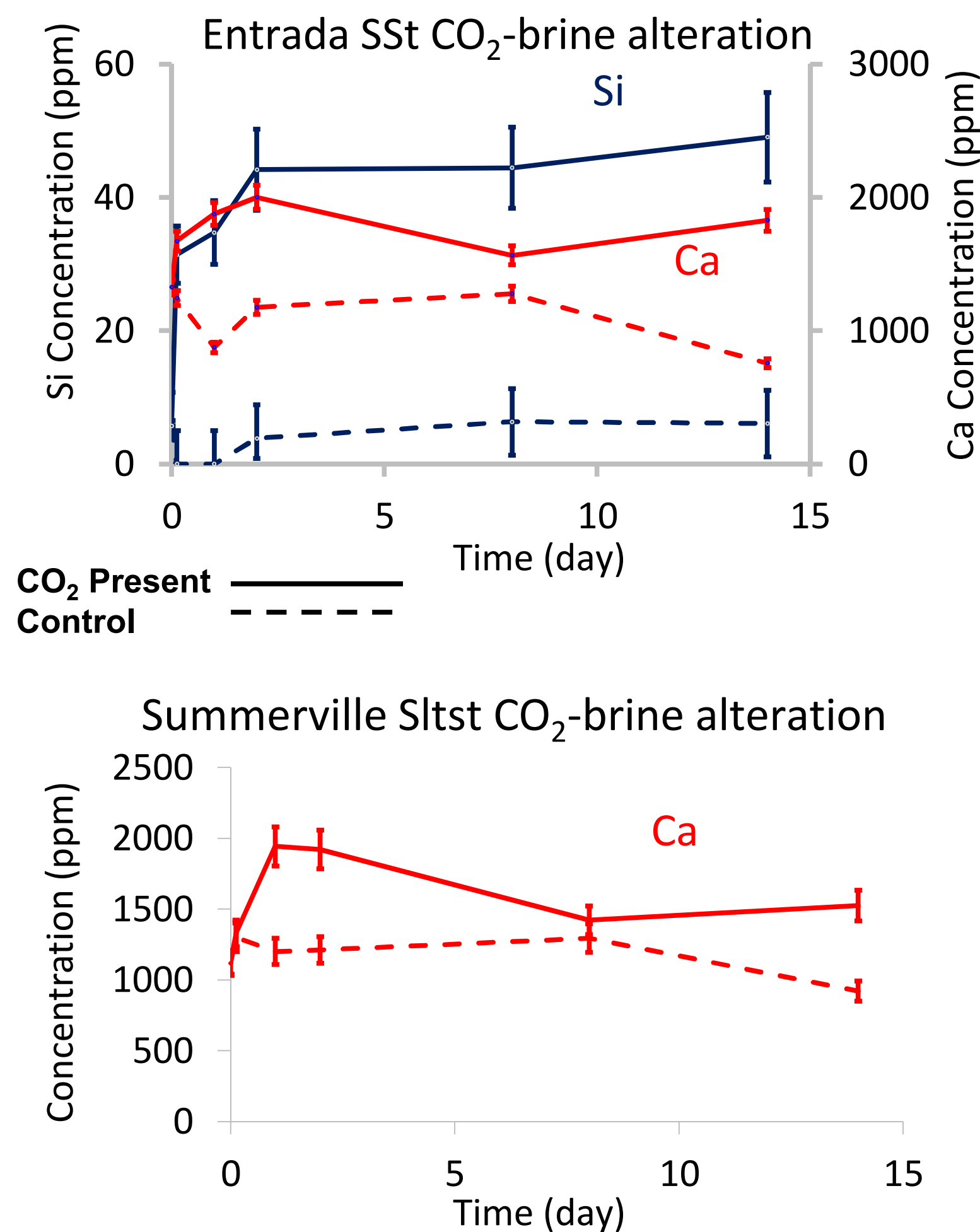
Scratch toughness K_S results for Entrada sandstone and Summerville siltstone. K_S values are calculated across 2-5mm length scratches and averaged. Error bars represent 1σ. For a linearly elastic isotropic material, the scratch toughness is equivalent to fracture toughness in the fracture driven regime (Akono & Kabir, 2016).

Results – X-ray Microscopy



Results – Analytical Geochemistry

Aqueous samples were collected at intervals of reaction time, preserved, diluted to 1000-1500x depending on the analysis method, and analyzed with ICP-MS using a Nexion 350D and for cations and anions with a Dionex ICS-1100.



Ion concentrations of Ca²⁺, analyzed by ion chromatography, and Si 28, analyzed by ICP-MS, for supercritical CO₂-brine alteration reactions with powdered Entrada Sst (top) and Summerville Siltst (bottom). Solid lines represent experiments with CO₂ present and dashed lines represent control water baths with no CO₂ and all other conditions held constant. Error bars represent cumulative uncertainty from dilution, calibration, and analysis. Additional analyses were completed for Na, K, Mg, Li, Cl, SO₄, and PO₄; no significant differences from the control reactions were observed. Initial synthetic brine concentrations followed the table displayed in the Geochemical Modeling section.

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 CO₂-charged brine.

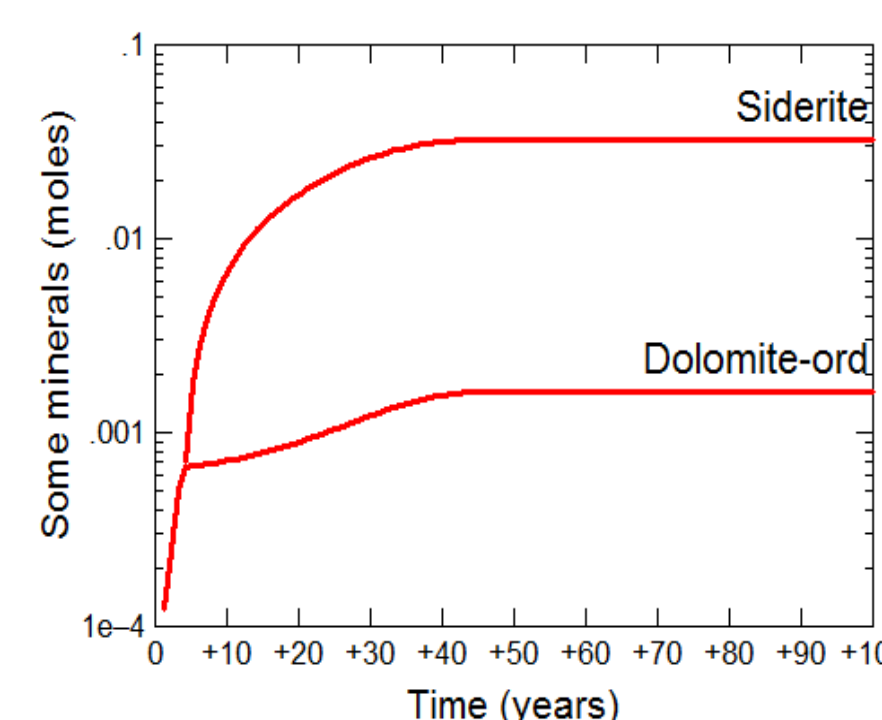
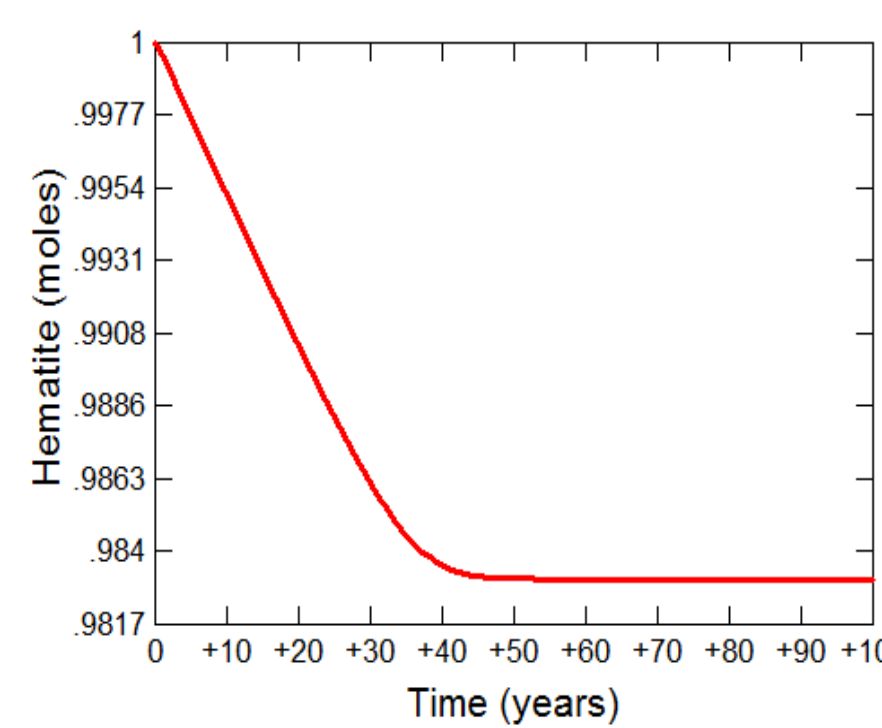


Fig.8. Numerical model: alteration of Entrada sandstone by CO₂-charged brine. Hematite dissolution (top), and siderite and dolomite precipitation (bottom) are predicted.

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 CO₂ and CH₄, and minerals quartz, K-feldspar, calcite, and hematite. The concentrations of CO₂ and CH₄ in the reactive fluid are chosen based on Wigley et al., 2012.

Conclusions & Ongoing Work

- Exposure of Entrada Sst and Summerville Siltst to reactive CO₂-brine mixtures over geological time frames resulted in mechanical degradation as shown by decreases in fracture toughness.
- Mechanical property trends determined from scratch tests validate previous double torsion fracture tests performed on same-source rock samples.
- Brine-CO₂ alteration of Entrada Sst and Summerville Siltst result in measurable dissolution of calcareous and silicate minerals, based on increases in Ca²⁺ and Si⁴⁺ across laboratory time scales with respect to brine-only control alteration.
- Further validation is required to determine whether geological heterogeneity, measurement error, and calibration inaccuracies are possible sources for variations in scratch toughness.
- Ongoing alteration experiments and corresponding micromechanical tests will investigate the alteration of Entrada Sst, Summerville Siltst, Mancos and Woodford shales, and Castlegate and Cranfield Sst with brine and deionized water autoclave fluids.

Acknowledgements

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References

- Akono, A.-T., & Kabir, P. Mech. Re. Commun. (2016). <http://dx.doi.org/10.1016/j.mechrescom.2015.12.003>
 Akono, A., Randall, N., & Ulm, F. (2012). *Journal of Materials Research*, 27(2), 485-493.
 Bethke, C. (1998). *The Geochemist's Workbench 8.0*. University of Illinois at Urbana-Champaign, IL.
 Harding, D.S., Oliver, W.C., & Pharr, G. (1995). *Mater. Res. Soc. Symp. Proc.* 356, 663 (1995).
 Carroll, S., McNabb, W., & Torres, S. (2011). *Geochemical Transactions*, 2011(12), 9-9.
 Carroll, S. et. al. (2013). *International Journal of Greenhouse Gas Control*, 16(1), S185-S193.
 Kim, S., & Santamarina, J. C. (2014). *Greenhouse Gases: Science and Technology*, 4(4), 528-543.
 Lu, J., et. al. (2012). *Chemical Geology* 291, 269-277.
 Major, J.R., et. al. (2014). *American Rock Mechanics Association*, 14-7463.
 Oliver, W., & Pharr, G. (2004). *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). *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., et. al. (2012). *Geology* 2012, 40, (6), 555-558.