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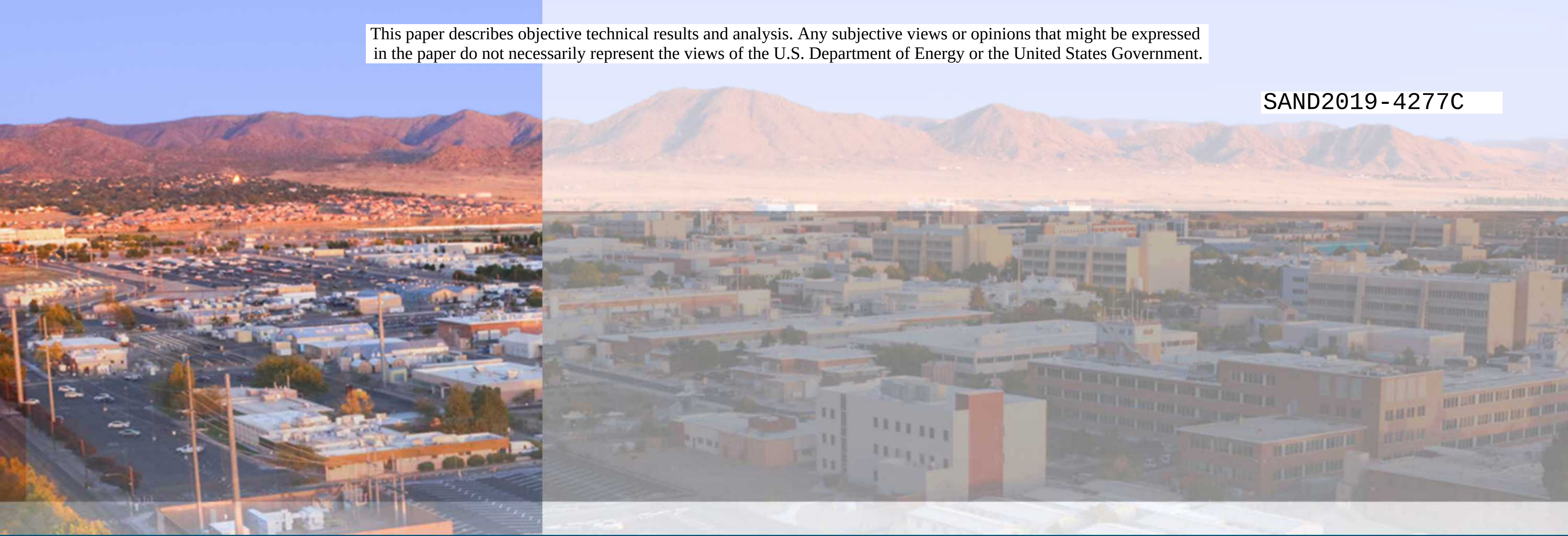

Chemical effects on fracture in calcite single crystals and in carbonate-rich shale

Anastasia G. Ilgen

Geochemistry Department

Sandia National Laboratories

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Today's talk

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Chemical controls on the propagation rate of fracture in calcite

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

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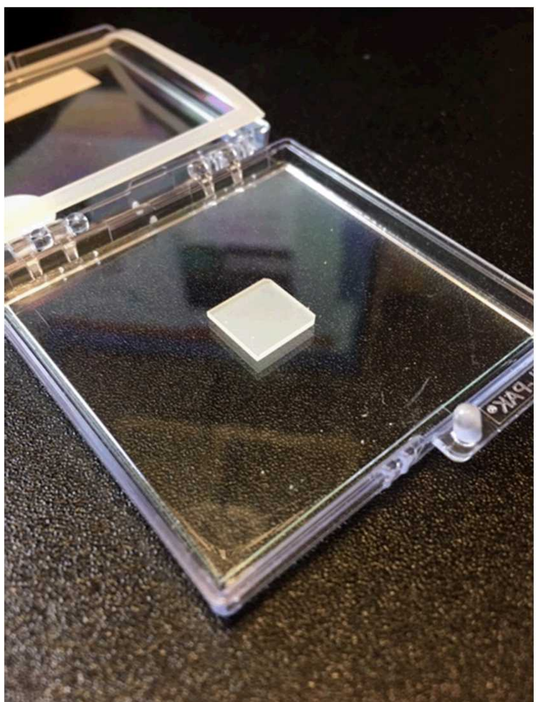


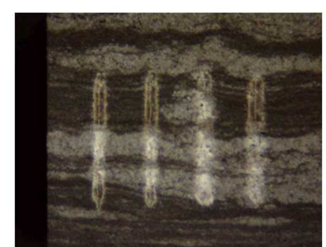
micron→centimeter

minutes→months

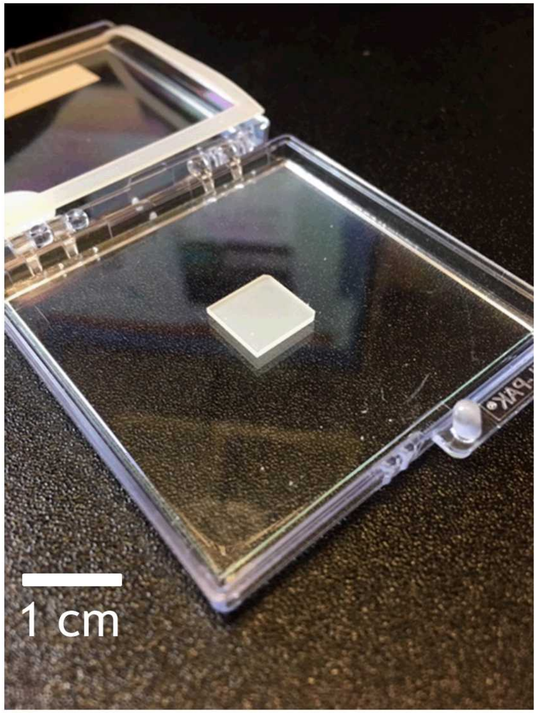
single crystal→shale

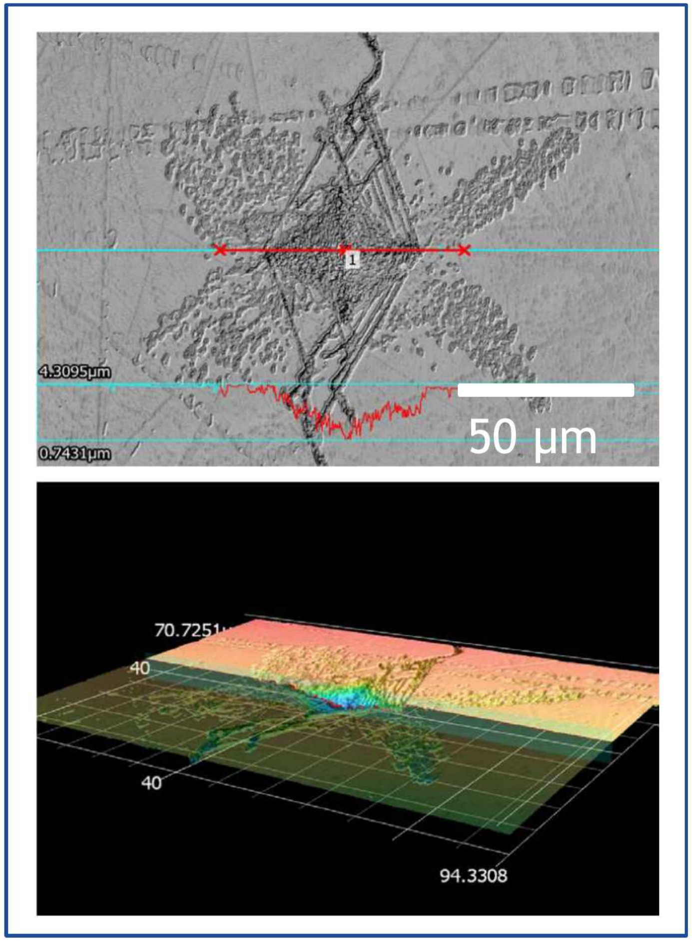
simple aqueous solutions →brine+scCO_2

Mancos Shale



Part I:
Chemical controls on subcritical fracture in calcite





Theory of subcritical fracture

Griffith theory:

$$U = (U_E - W_L) + U_S$$

the internal energy of the system (U), the elastic potential energy (U_E), the external work (W_L), the energy from the added surface area of the crack (U_S) [1].

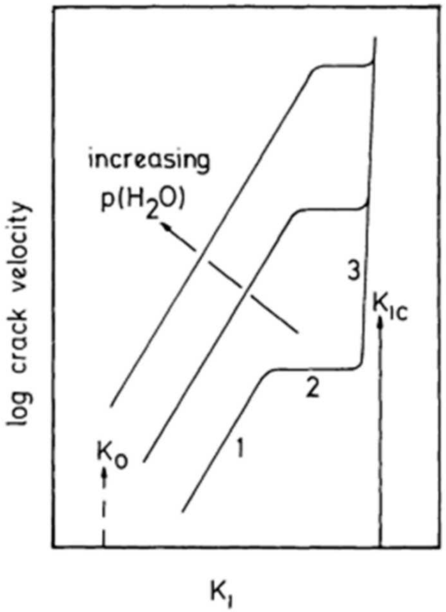
Constitutive modeling of subcritical crack growth:

Reaction rate theory

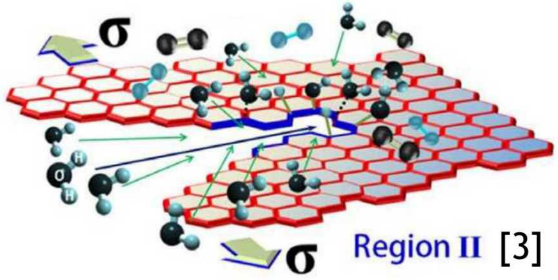
$$ln\left(\frac{r}{r_o}\right) = a - \left(\frac{E^* - v^* \sigma_{rs}}{RT}\right)$$

Where r is reaction rate, r_o and a - empirically determined constants, R – gas constant, T – absolute temperature, σ_{rs} is the reaction site stress, and E^* and v^* are apparent activation energy and activation volume.

Atkinson and Meredith, 1987



Schematic stress intensity factor/crack velocity diagram for tensile crack growth by stress corrosion. Kic is the fracture toughness and Ko is the stress corrosion limit [2].

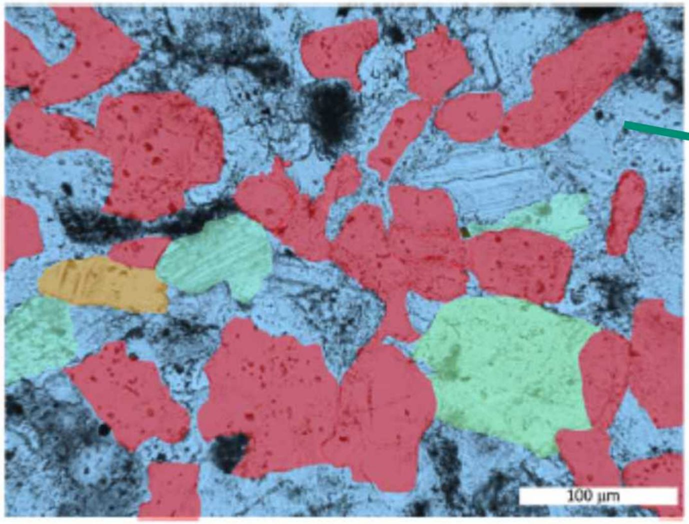


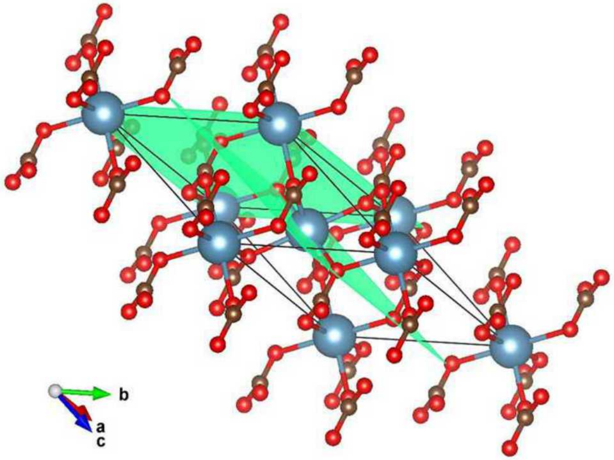
[3]

[1] Griffith, 1921
[2] Atkinson, 1984
[3] Hwangbo et al., 2014

Subcritical fracture in calcite

- Fractures can propagate through intergranular cement, or through mineral grains. Calcite ($CaCO_3$) cement is common in sandstones and mudrocks;
- Previous studies on subcritical fracture in calcite show that:
  - Activity of H_2O controls weakening of chalk [1]
  - Dissolution at fracture tip controls fracture growth [2,3]
  - Changes in surface energy control fracture propagation [4, 5]
  - In NaCl and NH_4Cl both weakening (faster fracture growth) and strengthening (fracture arrest) are observed [6]



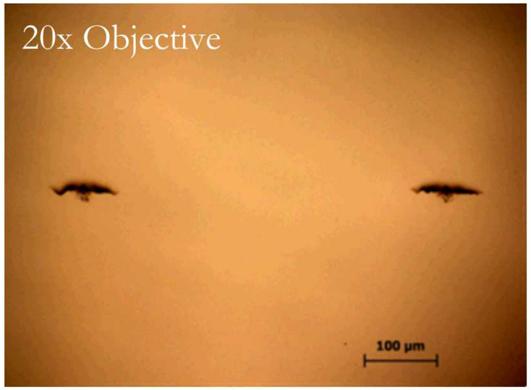


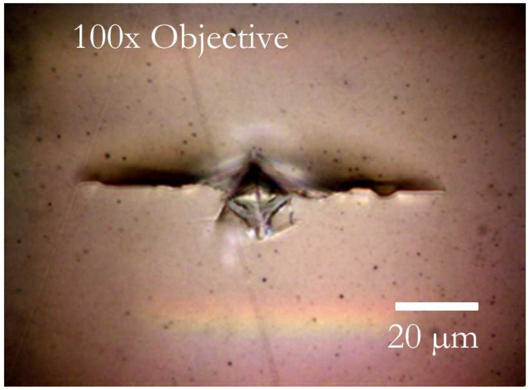
[1] Risnes et al., 2005
[2] Atkinson, 1984
[3] Royne et al., 2011
[4] Dunning et al., 1994
[5] Dunning et l., 1994
[6] Rostom et al., 2012

Project objectives and approach

To develop a mechanistic understanding of the chemical processes at the fracture tip in calcite and their control on subcritical fracturing.

Calcite Indentation, Vickers tip, 400 mN





Vickers tip

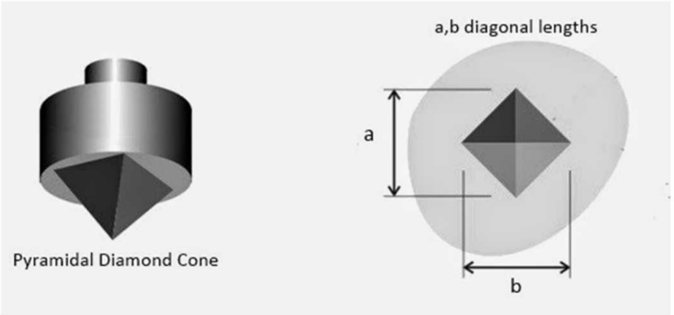


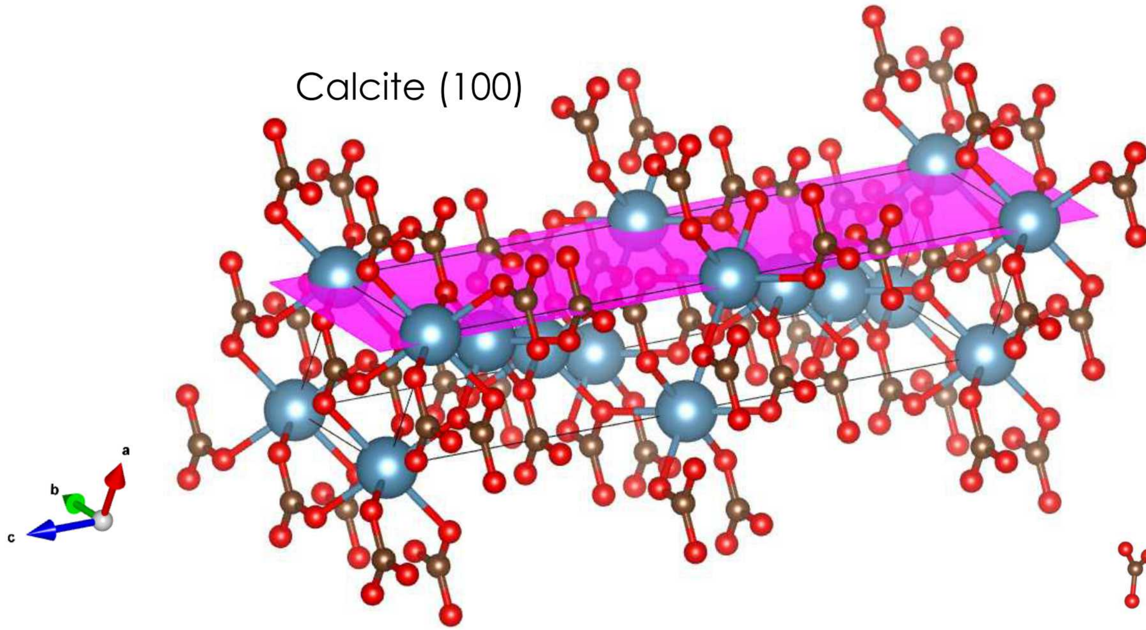
Image from: http://www.weldpedia.com/2014/10/macroscopic-and-microscopic-examination.html

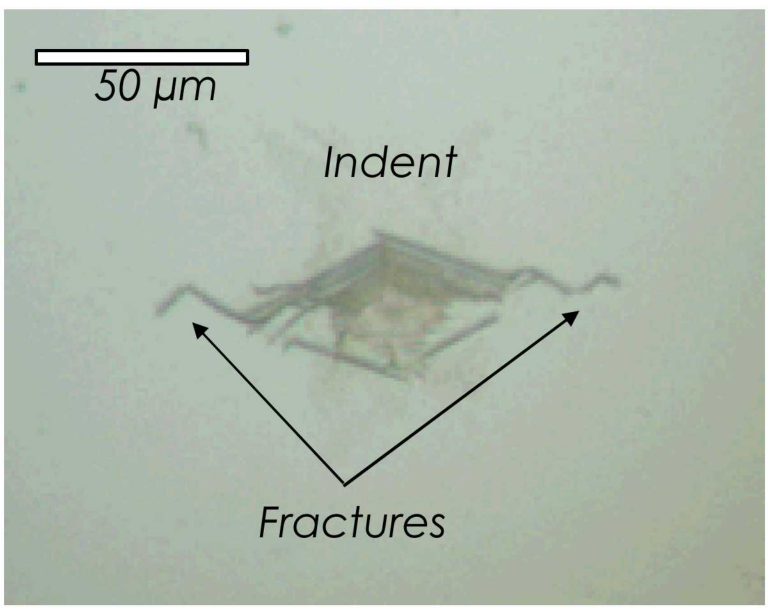
- Laboratory experiments to measure fracture propagation rate *in situ* as a function of chemical composition of the fluid;
- Single crystal calcite (100) indented using Vickers indenter tip at 400 mN force;
- Fractures are imaged *in situ* using optical microscope Nikon Eclipse 80i and SPOT 7.2 camera.

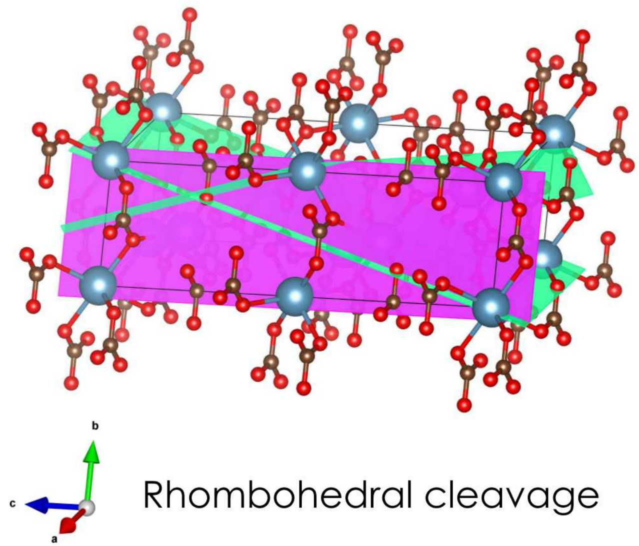
Results: fracture propagation

Crystal structures visualized using VESTA 3 (Momma and Izumi, 2011).

Calcite (100)





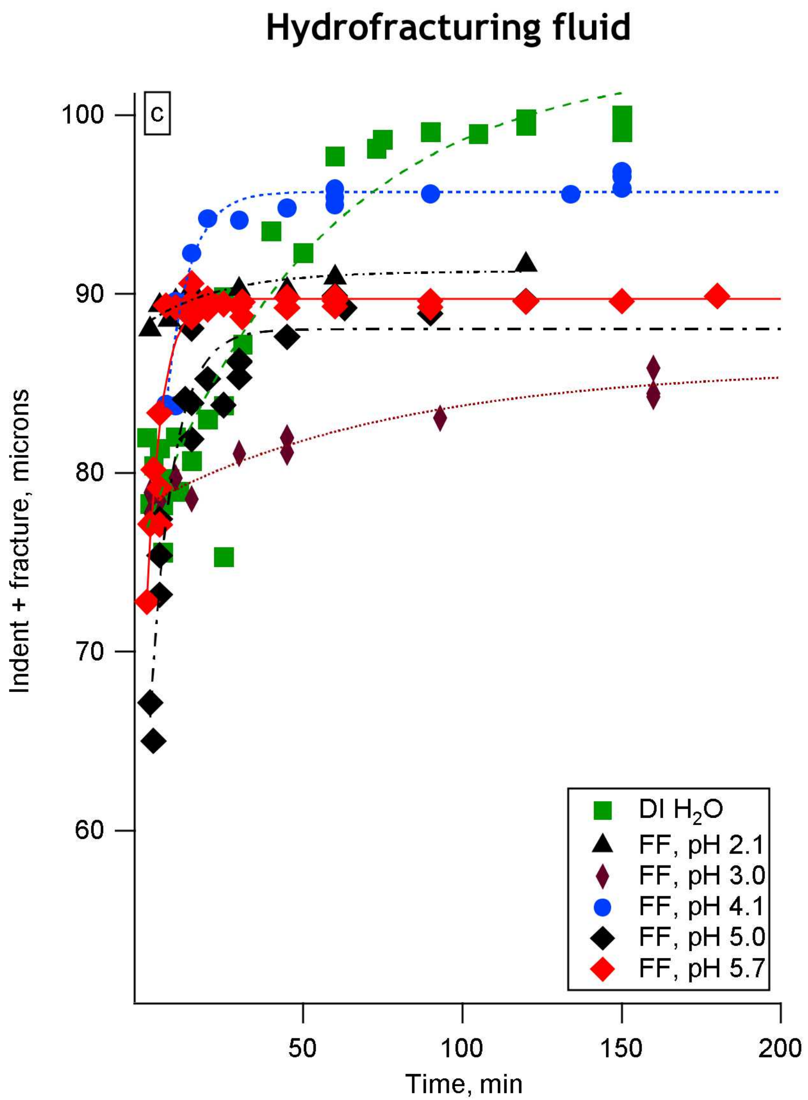


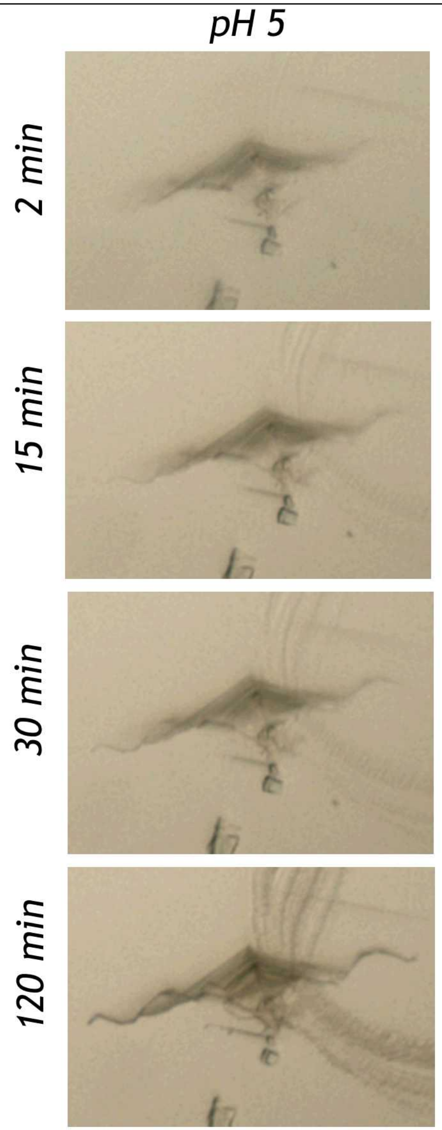
Rhombohedral cleavage

Ilgen, et al., 2018

Scientific Reports, 8, 164656.

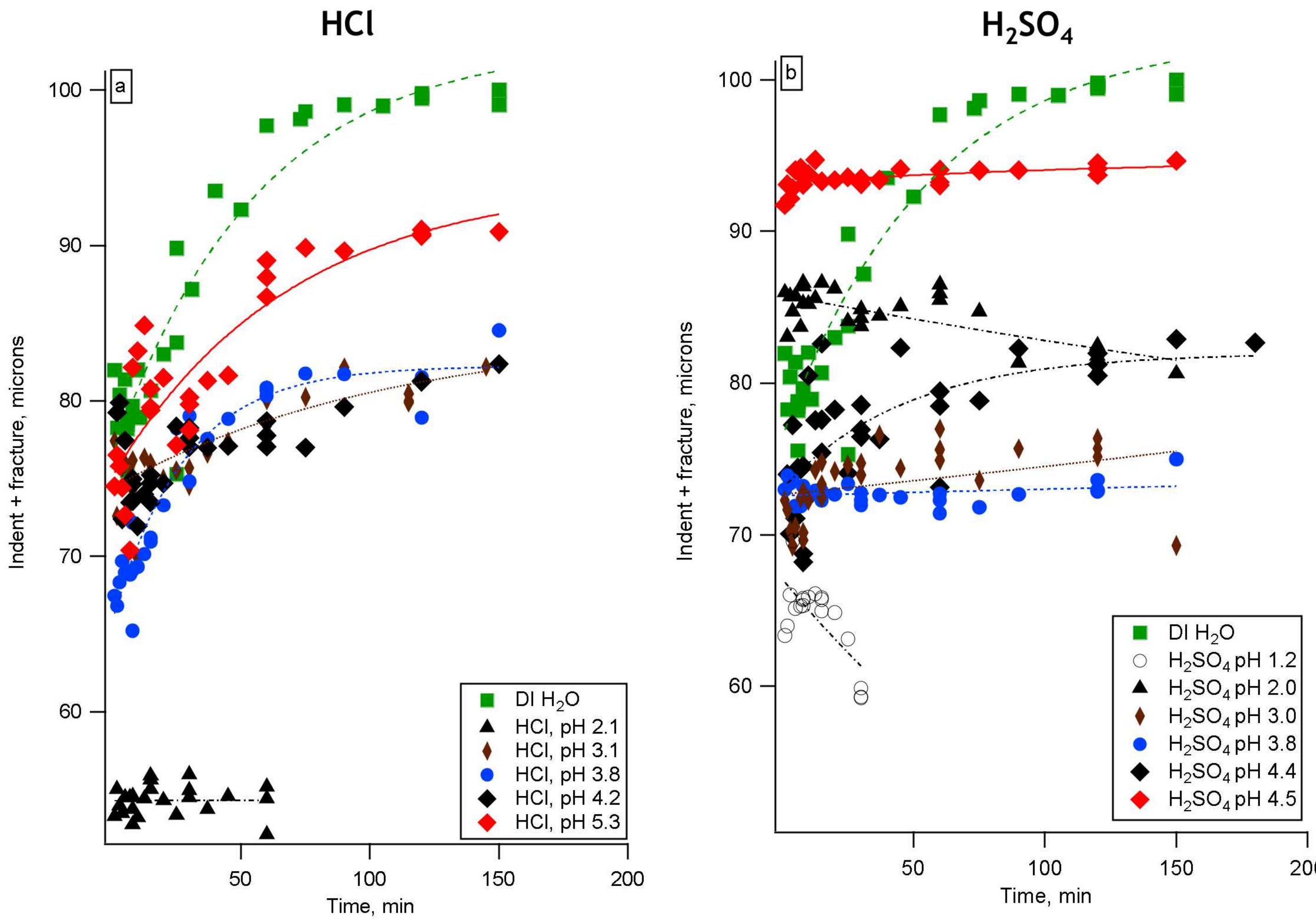
Results: fracture growth rate





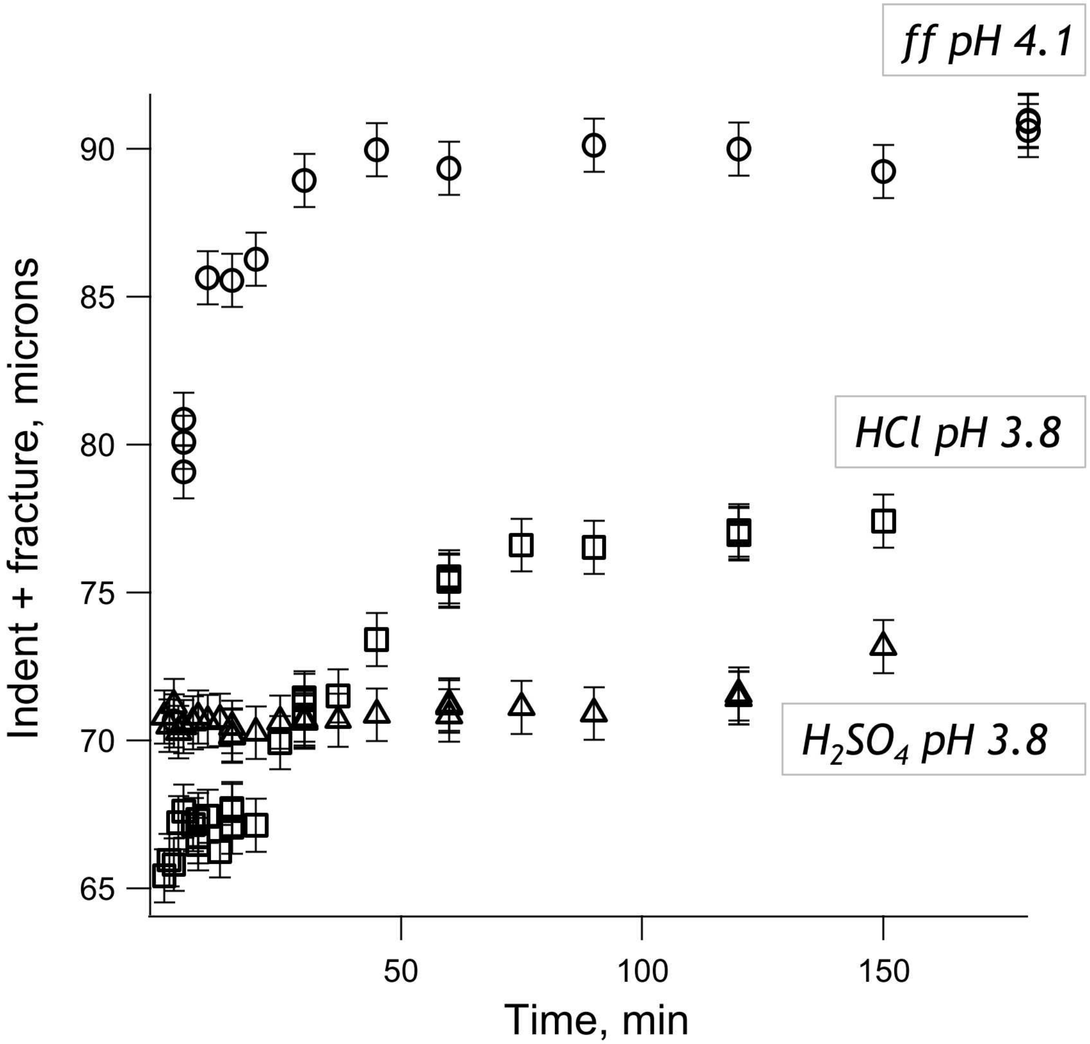
Synthetic hydrofracturing fluid: 0.01 vol.% Polyacrylamide; 0.05 vol.% Sodium polyacrylate; 0.1 vol.% Sodium chloride; 0.02 vol.% Methanol; 0.01 vol.% Hydrochloric acid; 0.007 vol.% Tetrakis(hydroxymethyl)phosphonium sulfate, 99.8 vol.% DI water.

Results: fracture growth rate



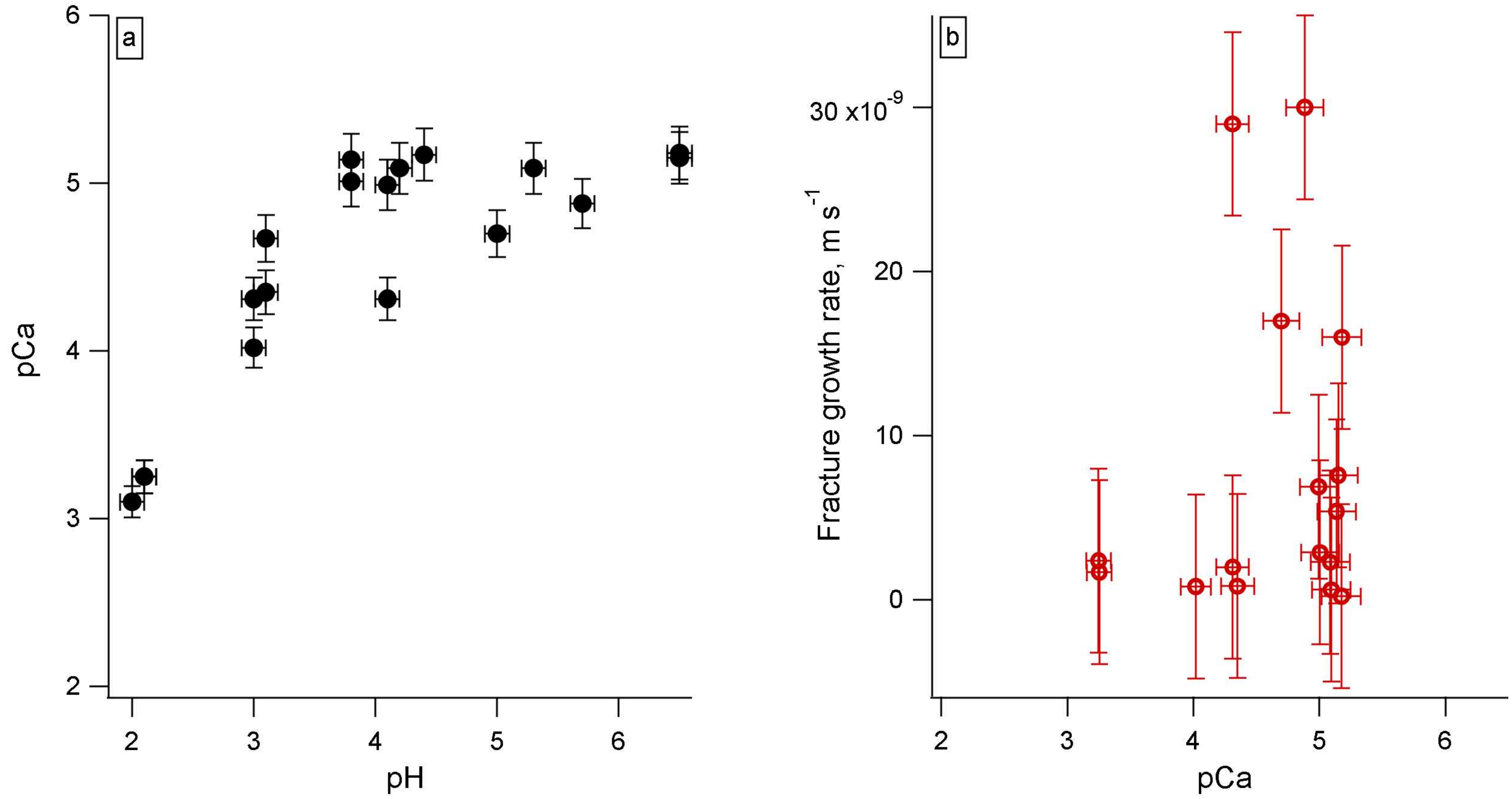
- The propagation rate of subcritical fracture measured *in situ* varied from 1.6×10^{-8} m s^{-1} to 2.4×10^{-10} m s^{-1}.

Results: what controls fracture growth?



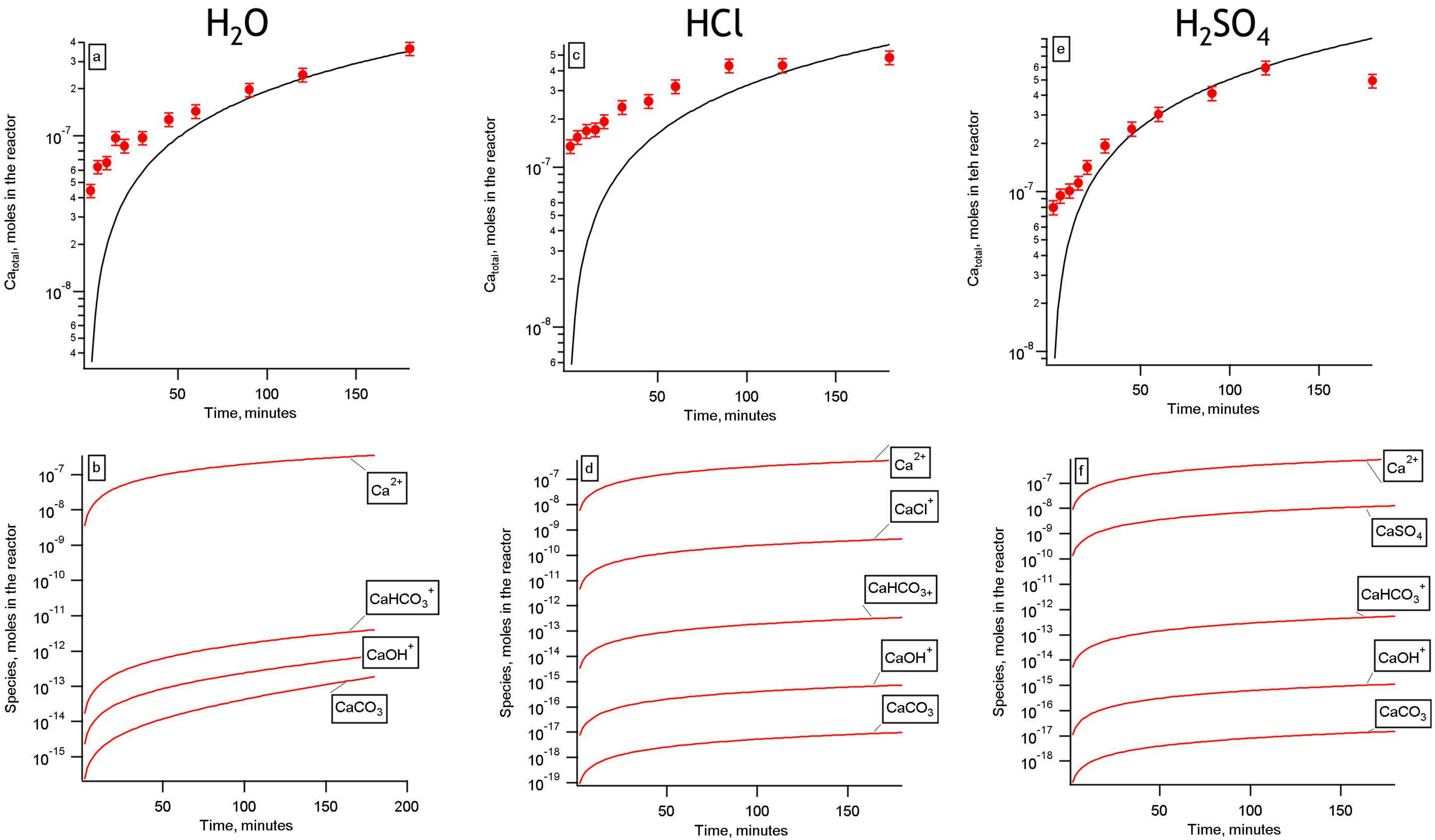
- Propagation rate of fracture in calcite is dependent on the anion.

Results: what controls fracture growth?



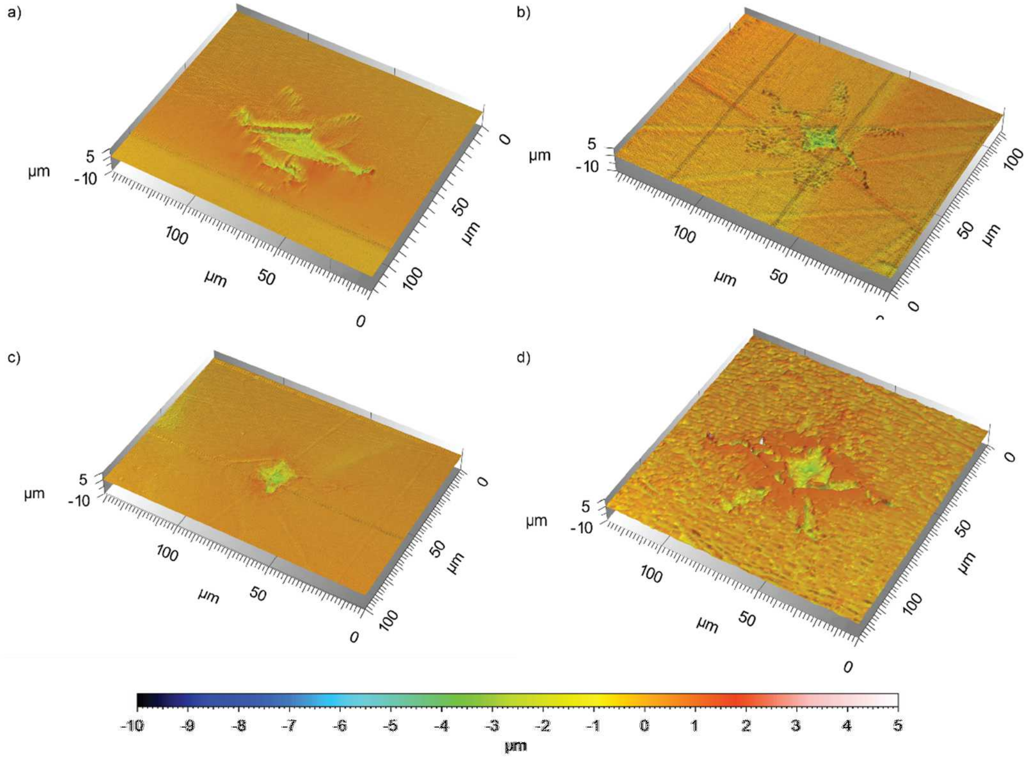
- No correlation between the dissolution rate of calcite and subcritical fracture growth.
- Positive correlation between pCa and pH for all examined reactors; pCa = $-\log_{10}[Ca^{2+}]$;
- No correlation observed between pCa (proxy for the ξ-potential) and fracture propagation rates.

Results: what controls fracture growth?



K_β for $CaCO_3$ is $10^{-7.128}$; K_β for $CaCl^+$ is $10^{0.7}$; and K_β for $CaSO_4$ is $10^{2.32}$

Results: surface morphology and fracture toughness



Fracture toughness [1]:

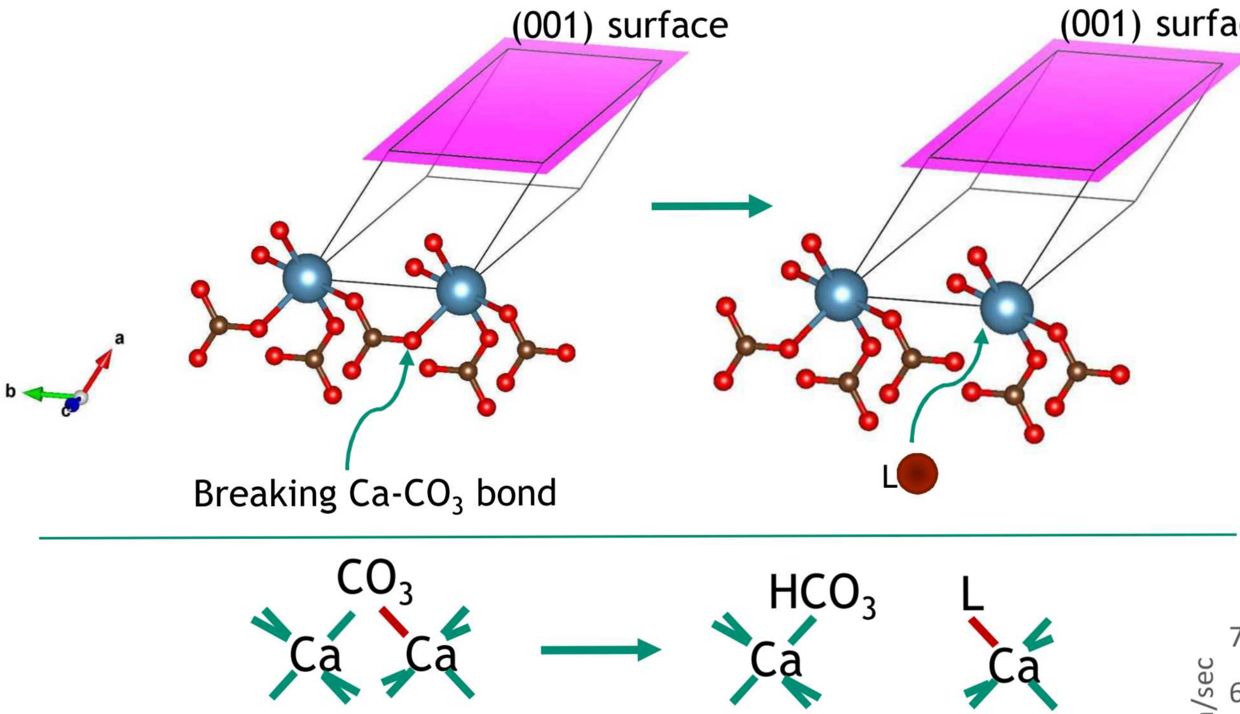
$$\frac{P}{c^{3/2}} = \frac{1}{\xi} \times \left(\frac{H}{E}\right)^{1/2} \times T$$

- The estimated fracture toughness prior to *in situ* fracture growth experiment was $0.10 – 0.16$ MPa $m^{1/2}$
- Fracture toughness at the end of the fracture growth experiment decreased by 0.01-0.05 units.

- The fracture width, measured on the surface of the sample, increased with decreasing pH, in agreement with enhanced calcite surface dissolution with decreasing pH.

[1] Lawn and Cook, 2012

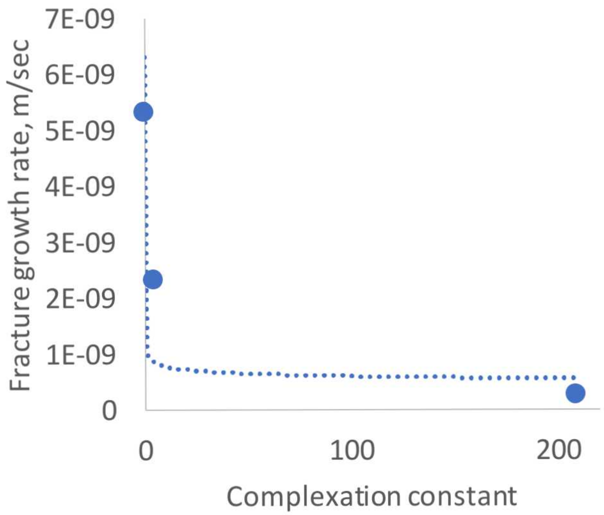
Results: Conceptual model



$$>Ca—OH + H_2CO_3 \rightarrow >Ca—CO_3^- + H^+ + H_2O$$

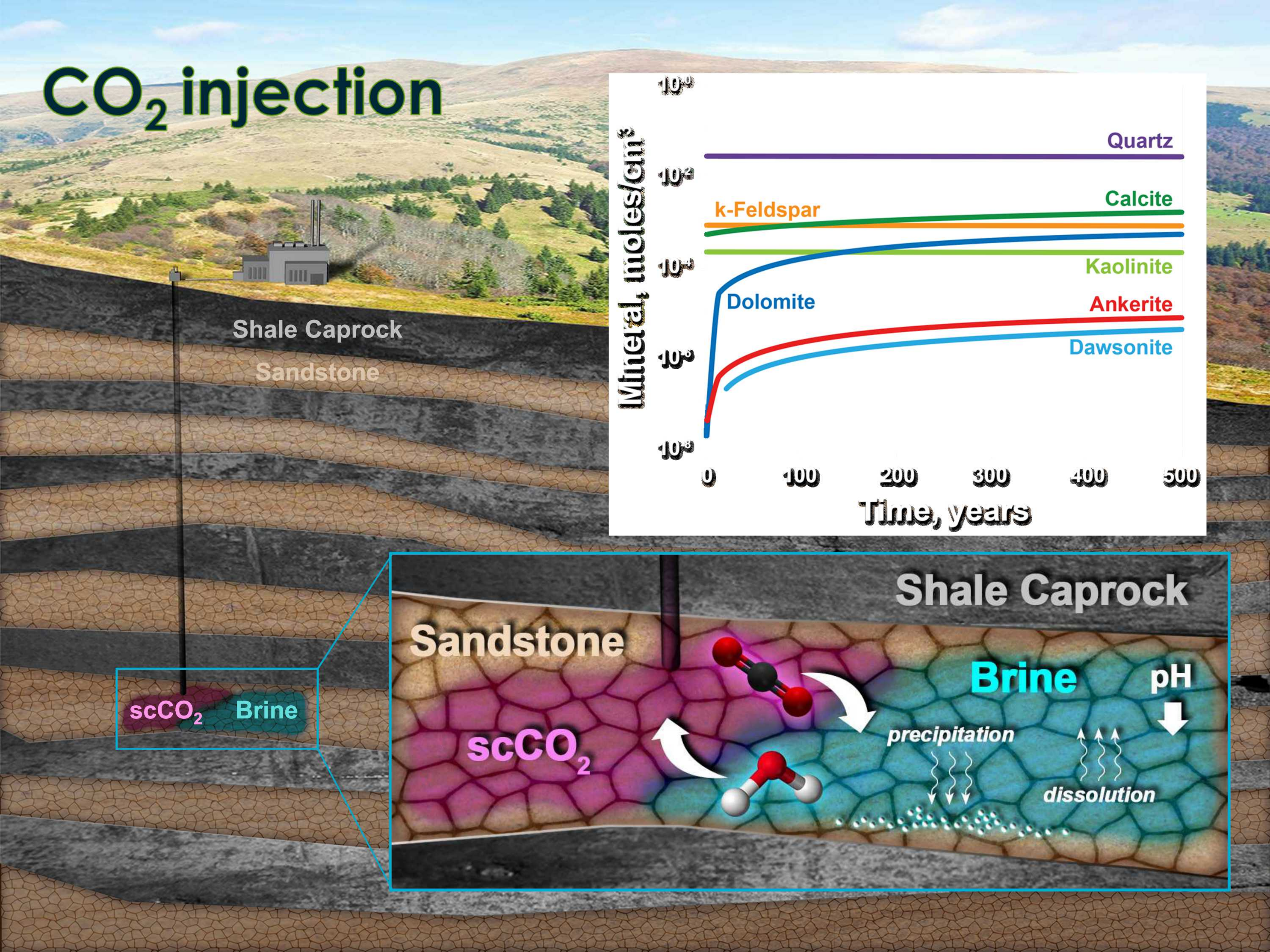
$$>Ca—OH + HCl \rightarrow >Ca—Cl + H_2O$$

$$>Ca—OH + H_2SO_4 \rightarrow >Ca—SO_4^- + H^+ + H_2O$$



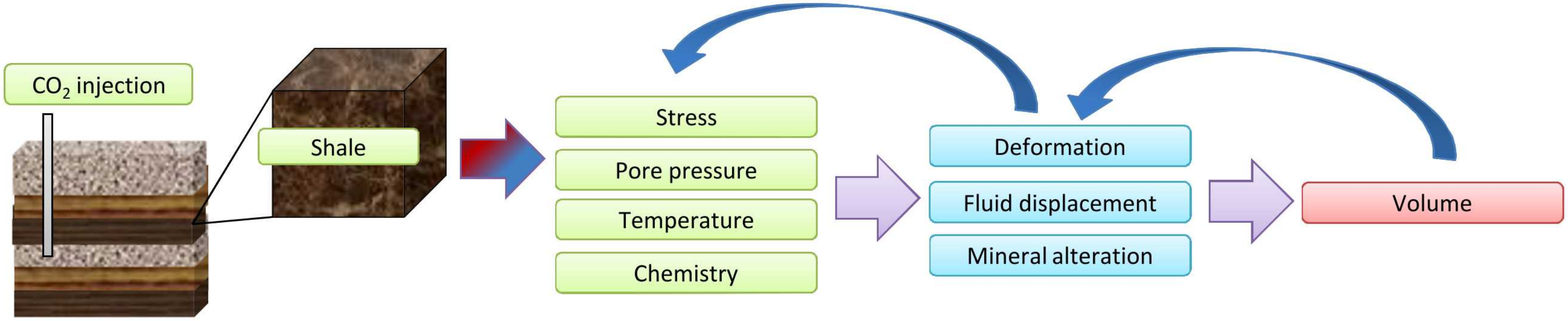
Part II:
Shale-brine-CO_2 interactions and the long-term stability of carbonate-rich shale caprock

Mancos Shale


CO2 injection
Quartz
Calcite
k-Feldspar
Kaolinite
Dolomite
Ankerite
Dawsonite
10^0
10^-2
10^-4
10^-6
10^-8
Mineral, moles/cm^3
0
100
200
300
400
500
Time, years
Shale Caprock
Sandstone
scCO2
Brine
Shale Caprock
Sandstone
Brine
pH
precipitation
dissolution
scCO2

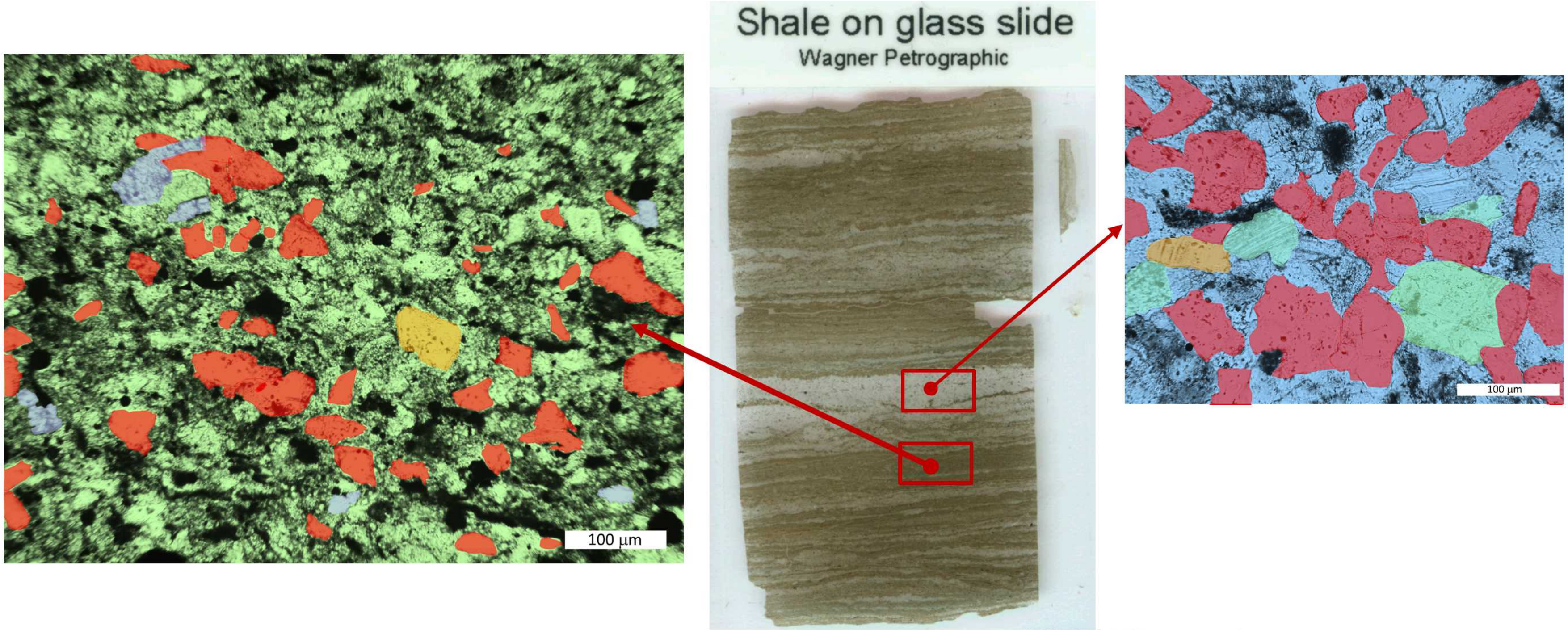
Geochemical response triggered by the injection of CO_2

- 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]

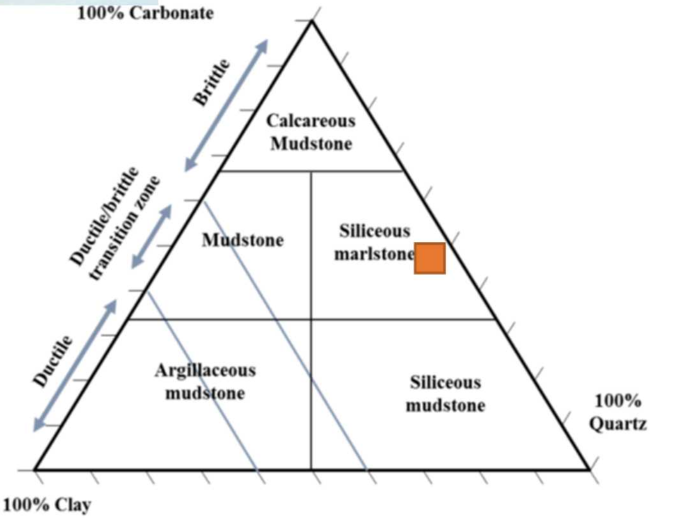


[1] DePaolo et al., 2013
[2] Marini, 2006
[3] Kharaka and Cole, 2011
[4] Kobos et al., 2011
[5] Steele-MacInnis et al., 2012
[6] Gilfillan et al., 2009
[7] Bickle et al., 2013
[8] Jun et al., 2012
[9] Lu et al., 2012
[10] Liu et al., 2012
[11] Kaszuba et al., 2003
[12] Harvey et al., 2012

Heterogeneous natural shale



- Petrography
- Micro-XRF
- Micro-XRD
- Bulk XRF, XRD

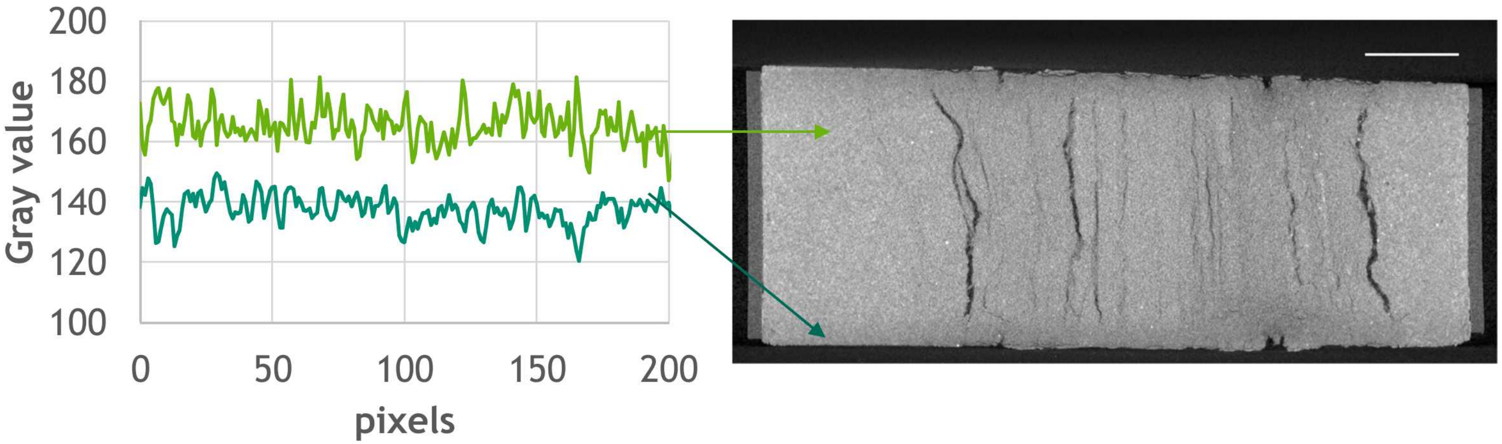


Ilgen, et al., 2018

Int. J. Greenh. Gas Contr. 78, 244-253.

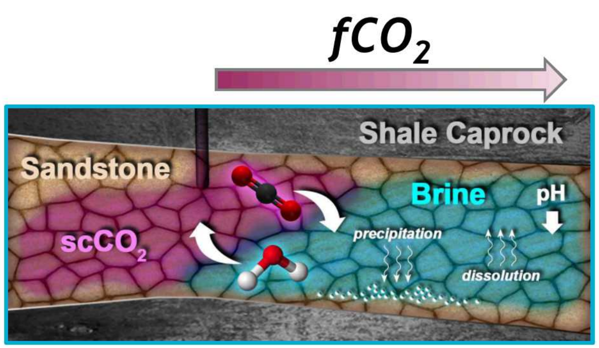
Project objectives

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



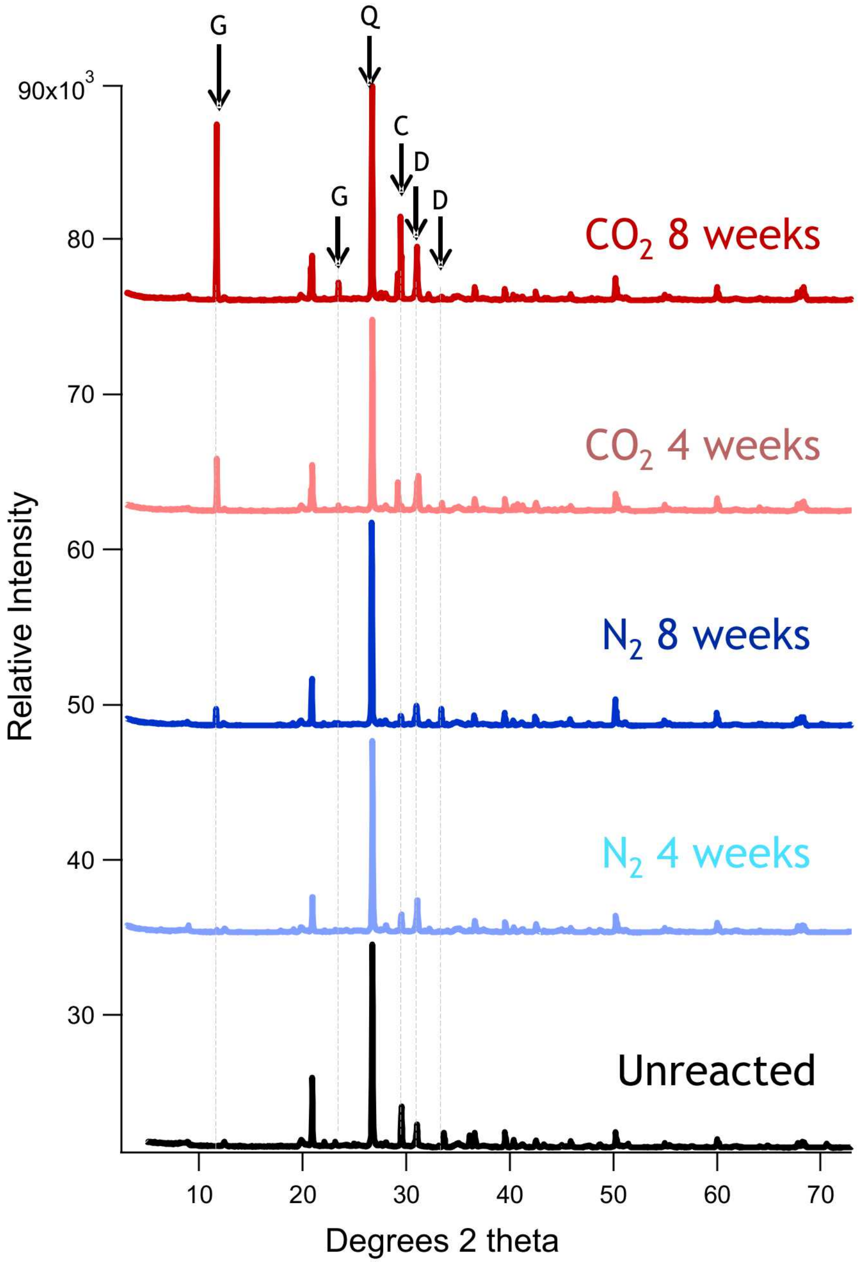
- Laboratory experiments on shale samples at conditions typical of GCS to understand time-dependent geochemical reactions.
- Geochemical modeling for data interpretation.
- Micro-mechanical characterization to understand chemical effects on mechanical properties in heterogeneous shale caprock.

Shale alteration in brine-CO_2 mixtures



- 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

Results: mineralogy changes

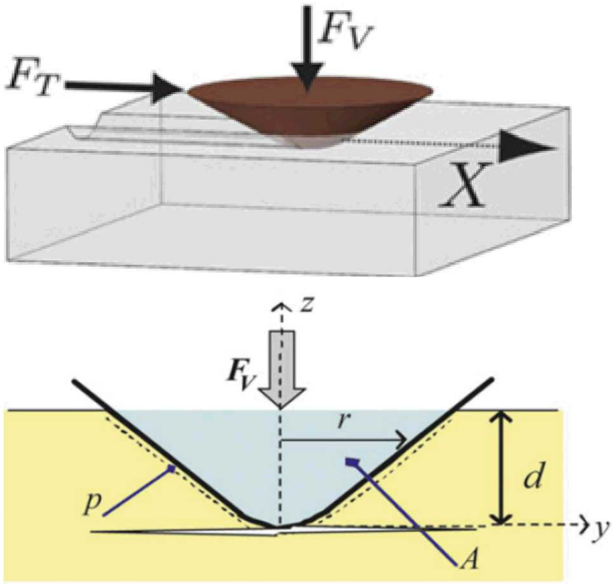


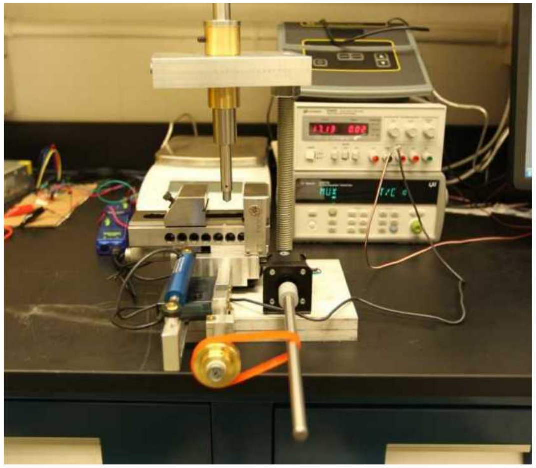
Mineral	Calcite	Albite	Dolomite	Muscovite
ρ, g cm^{-3}	2.71	2.62	2.84	2.82
Hardness	3	7	3.5 - 4	2 - 2.5
Mineral	**Calcite**	**Gypsum**	**Magnesite**	**Gibbsite**
ρ, g cm^{-3}	2.71	2.3	3	2.42
Hardness	3	2	4	3

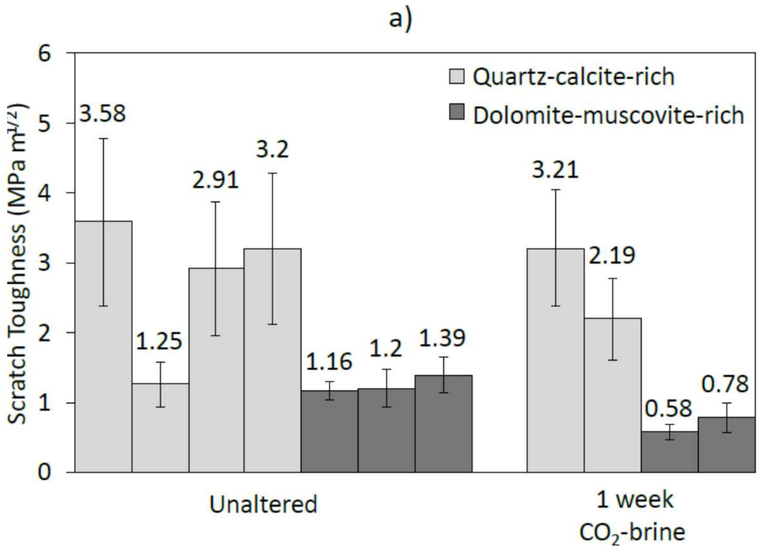
Alteration by CO_2-brine mixture maybe causing net decrease in density and hardness.

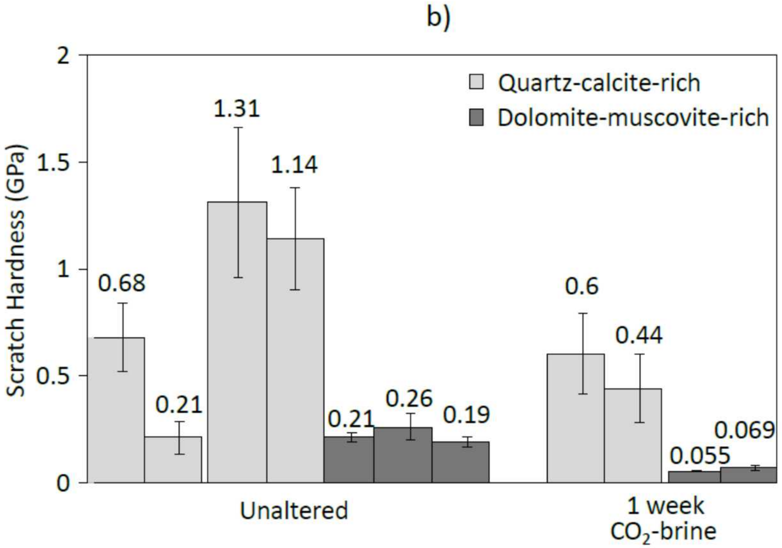
Does this have consequences for micro-mechanical properties?

Fracture Toughness: Scratch Test









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

Mancos shale: Conclusions

Low pCO_2 reactor:

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

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

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

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

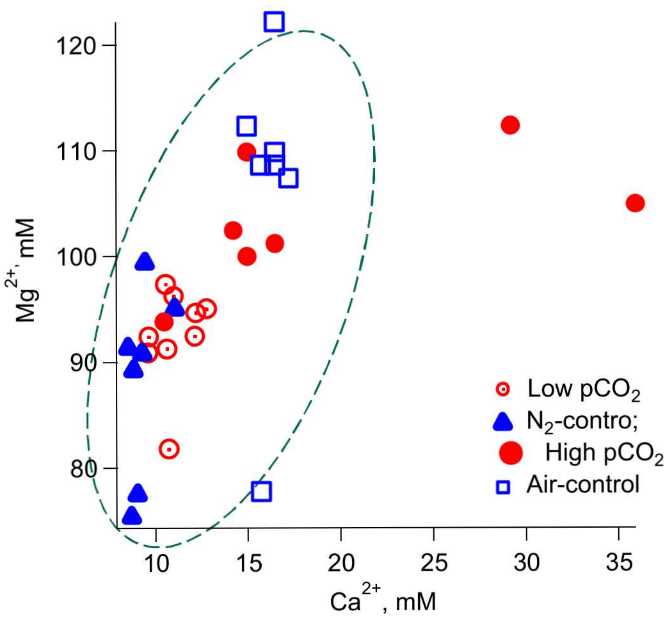
High pCO_2 reactor:

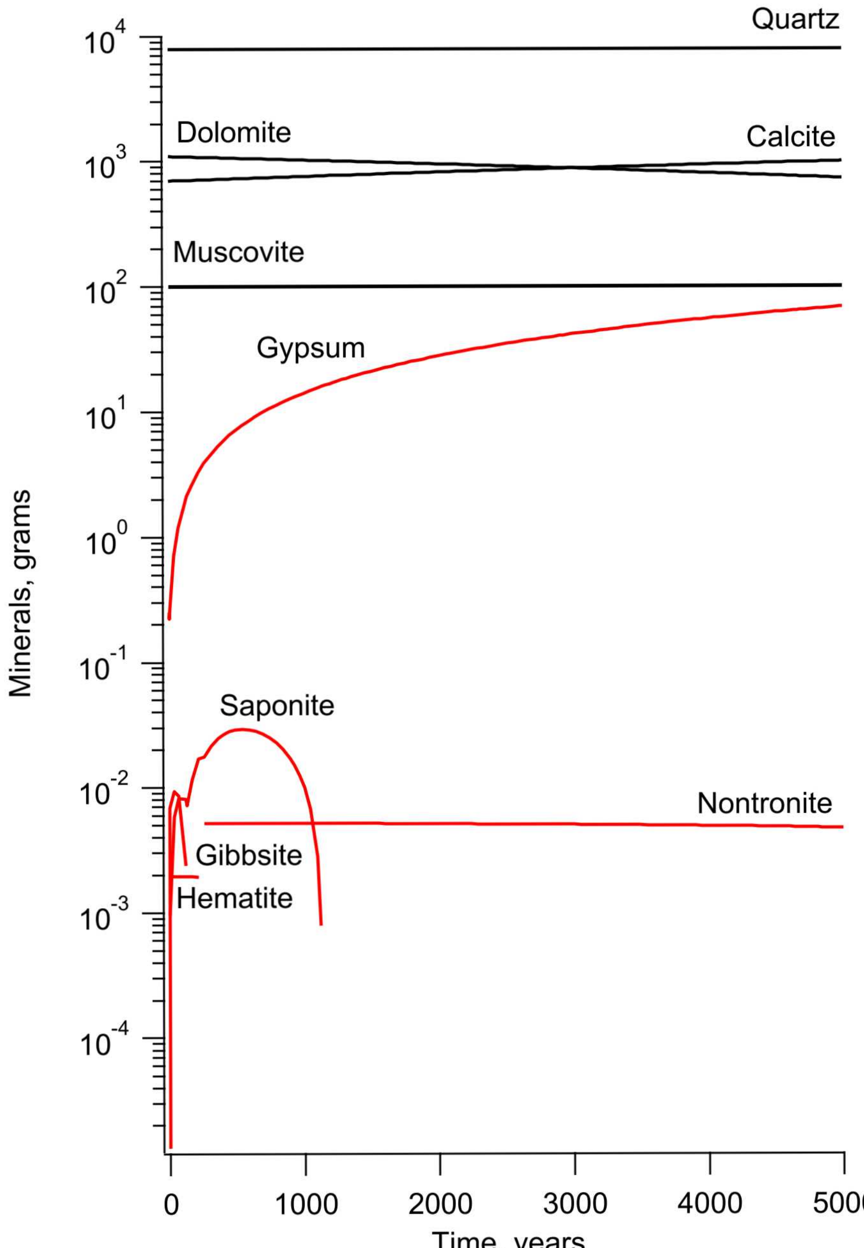
$CaCO_{3(s)} + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$

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

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

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

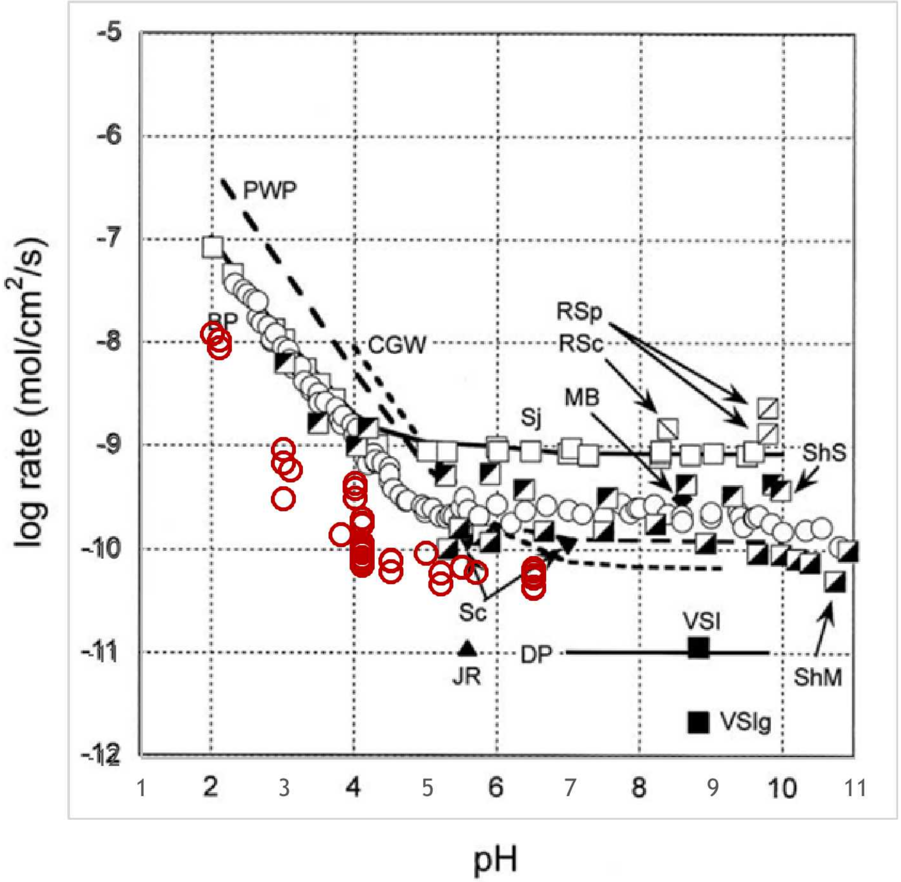




Thank you.

Calcite dissolution kinetics

Calcite dissolution rates

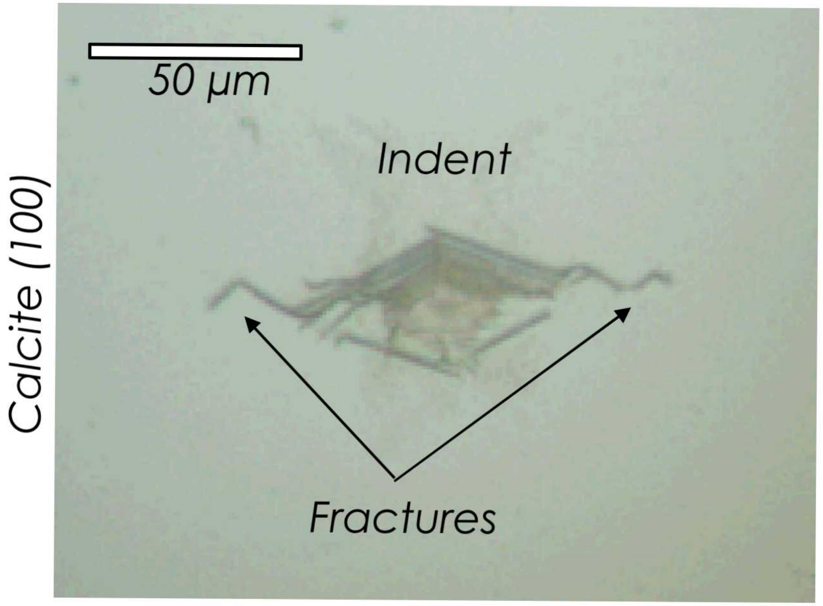


Arvidson et al. (2003) Geochimica et Cosmochimica Acta, 67, 8, 1623

Initial (incorrect) hypothesis:
Propagation rate of fracture is controlled by the dissolution rate of calcite

Experiment matrix

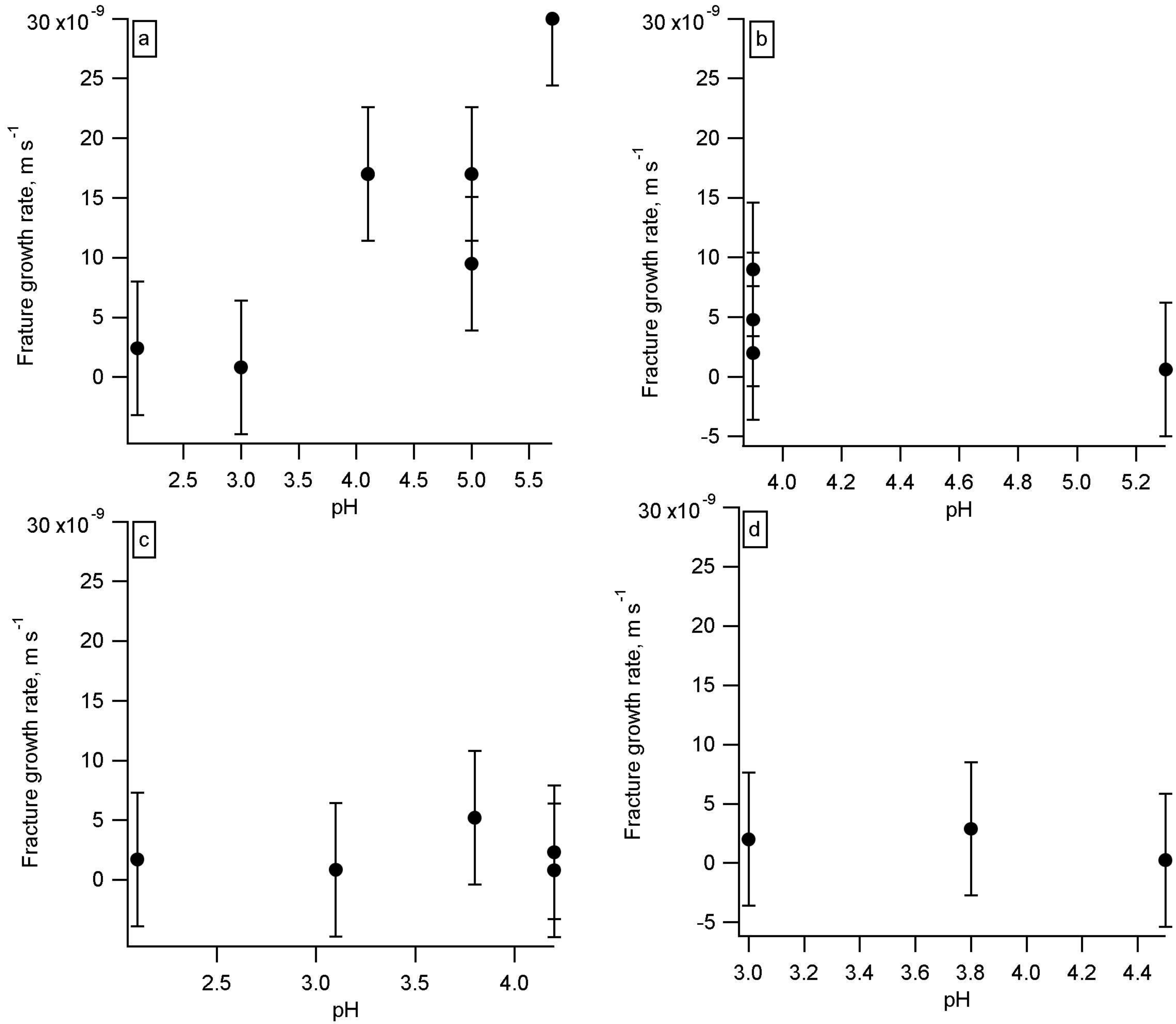
Hydrofracturing fluid	pH=5.72	pH=5.02	pH=4.07	pH=3.02	pH=2.07	pH=1.08
HCl	pH=5.25	pH=4.18	pH=3.77	pH=3.12	pH=2.13	pH=1.21
H_2SO_4	pH=4.41	pH=4.53	pH=3.78	pH=3.04	pH=2.04	pH=1.35
$H_2C_2O_4$	pH=6.78	pH=5.26	pH=3.88	pH=3.07	pH=2.12	pH=1.49



- Samples: 2 x 2 mm, CaCO3 (100)
- Optical imaging *in situ*

Ilgen, et al., 2018

Scientific Reports, 8, 164656.


a
b
c
d
30 x10^-9
25
20
15
10
5
0
-5
Frature growth rate, m s^-1
Fracture growth rate, m s^-1
2.5
3.0
3.5
4.0
4.5
5.0
5.5
4.0
4.2
4.4
4.6
4.8
5.0
5.2
3.2
3.4
3.6
3.8
4.4
pH

Reactor	pH	Fracture length (initial), microns	Fracture length (final), microns	c [a] (initial), microns	c [a] (final), microns	T [b] (initial), MPa $m^{1/2}$	T [b] (final), MPa $m^{1/2}$
DI H_2O	6.5	89.2	98.8	44.6	49.4	0.10±0.01	0.09±0.01
DI H_2O	6.5	82.0	99.1	41.0	49.6	0.12±0.01	0.09±0.01
DI H_2O	6.5	73.6	93.4	36.8	46.7	0.14±0.02	0.10±0.01
FF	4.1	83.8	96.0	41.9	48.0	0.11±0.01	0.09±0.01
HCl	3.8	67.5	84.5	33.8	42.3	0.16±0.02	0.11±0.01
H_2SO_4	3.8	73.0	75.0	36.5	37.5	0.14±0.02	0.14±0.02
$C_2H_2O_4$	4.1	72.7	99.0	36.4	49.5	0.14±0.02	0.09±0.01

Table S1. Calculated fracture toughness before and after exposure to aqueous solutions. The uncertainty in fracture toughness value is ±0.01-0.02 (shown in parenthesis with each calculated T value), calculated at 2σ (95% confidence level).

Notes:

•C is calculated as ½ of the full fracture length

•T is fracture toughness