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Subcritical Fracturing of Calcite Single Crystals and Grain Packs

Anastasia G. Ilgen,[1] R. Charles Choens,[2] and Jennifer Wilson [2]

[1]Geochemistry Department; [2]Geomechanics Department

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NNSA National Nuclear Security Administration

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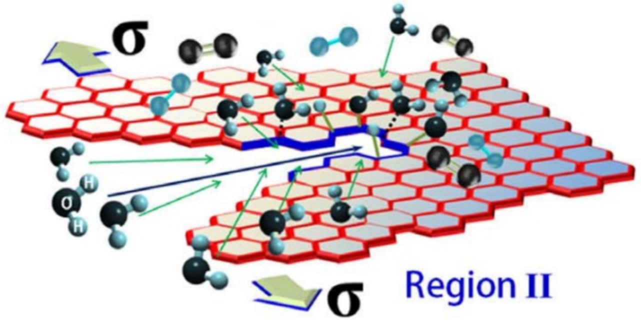
Overview: theory of chemically-assisted fracturing

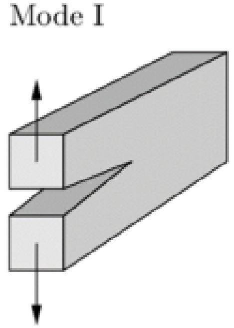
Griffith theory:

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

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).



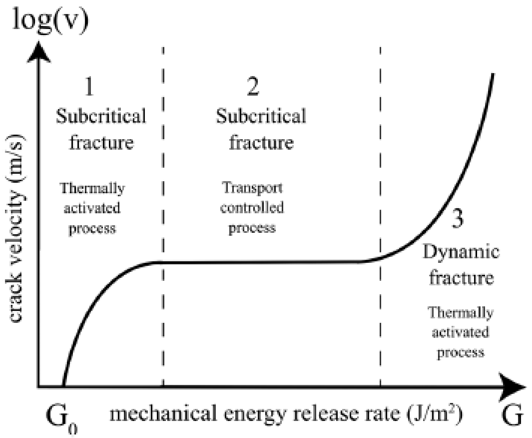
Hwangbo et al., 2014



Atkinson and Meredith, 1987

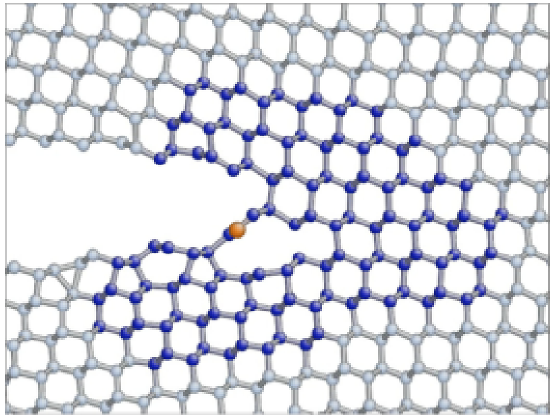
Constitutive modeling of subcritical crack growth:

$$v = 2\frac{kT}{h} a_0 \, exp\left(\frac{-\Delta F}{kT}\right) sinh\left(\alpha \frac{G - G_0}{kT}\right)$$

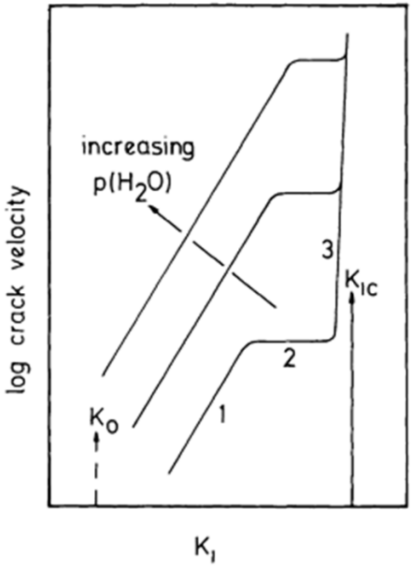


Bergsaker et al., 2016

v is crack velocity, k is Boltzmann's constant, h is Plank's constant, G is mechanical energy release (G_0 is theoretical limit), a_0 is characteristic atomic spacing, α is activation area, ΔF is apparent activation barrier.



Bitzek et al., 2005

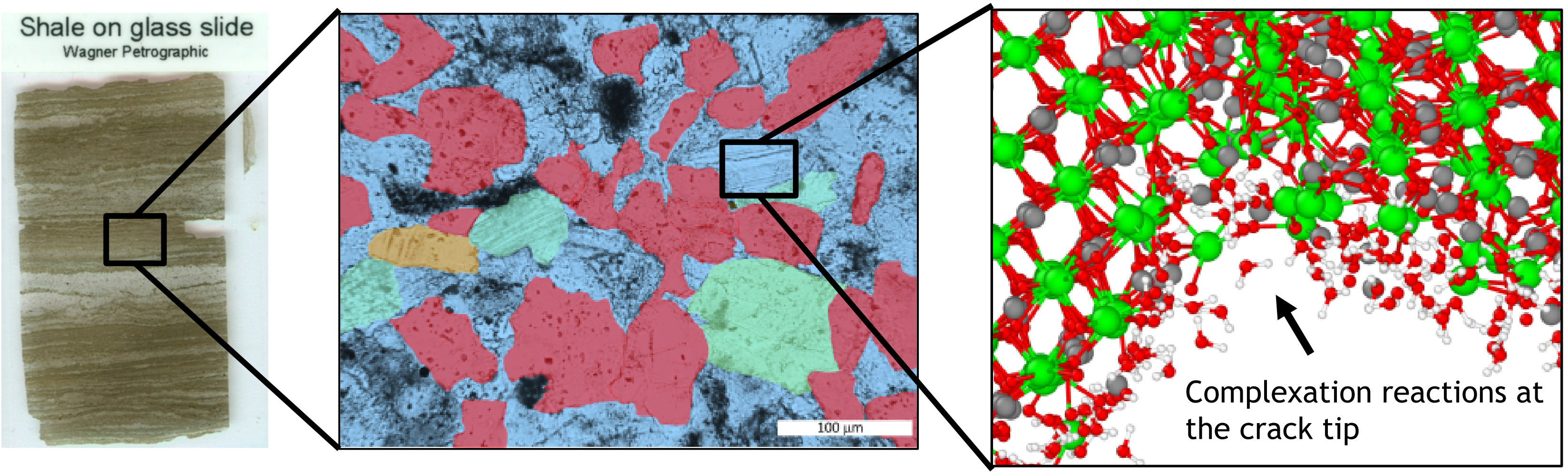


Schematic stress intensity factor (K_i) and crack velocity diagram for tensile crack growth by stress corrosion. K_{ic} is the fracture toughness and Ko is the stress corrosion limit.

Chemically-assisted fracturing in calcite: hypothesis

Science Question: How and why do chemical complexation reactions at a single crack tip change *in situ* fracture behavior?

Hypothesis: With increasing favorability of the cation-ligand complex, the velocity of subcritical crack growth decreases, and the effective fracture toughness increases.



- Fracturing in rocks can occur through intergranular cement, or through mineral grains. Calcite ($CaCO_3$) and quartz (SiO_2) cements are common intergranular phases in sedimentary rocks;
- Previous studies on subcritical fracture 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 [4-7]

[1] Risnes et al., 2005
[2] Atkinson, 1984
[3] Royne et al., 2011
[4] Rostom et al., 2012
[5] Griffith, 1921
[6] Kermode et al., 2013
[7] Bergsaker et al., 2016

Outline

SCIENTIFIC REPORTS

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Chemical controls on the propagation rate of fracture in calcite

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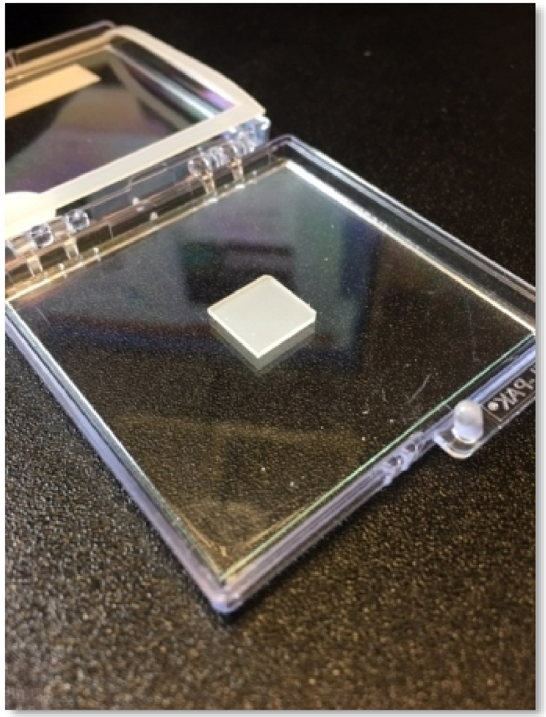
A. G. Ilgen[1], W. M. Mook[2], A. B. Tigges[1], R. C. Choens[3], K. Artyushkova[4] & K. L. Jungjohann[2]

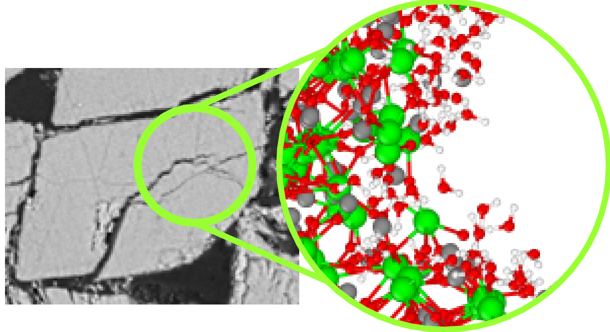


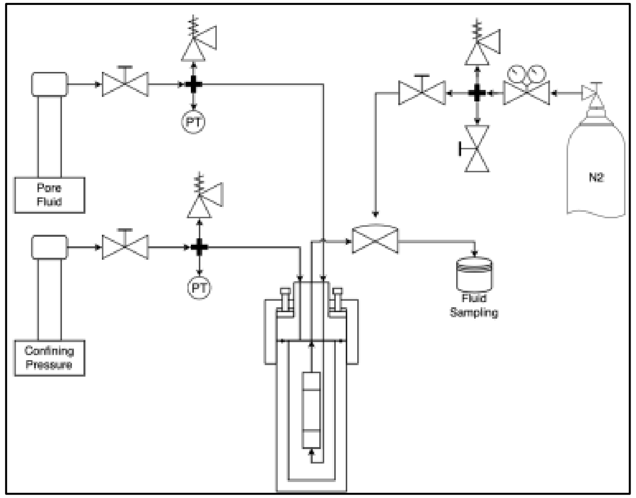
Submitted paper:

Strengthening of Calcite Assemblages through Chemical Complexation Reactions

R. C. Choens, J. Wilson, and A. G. Ilgen

- micron→centimeter
- minutes→days
- single crystal→grain pack
- dilute aqueous solutions →0.5M brines

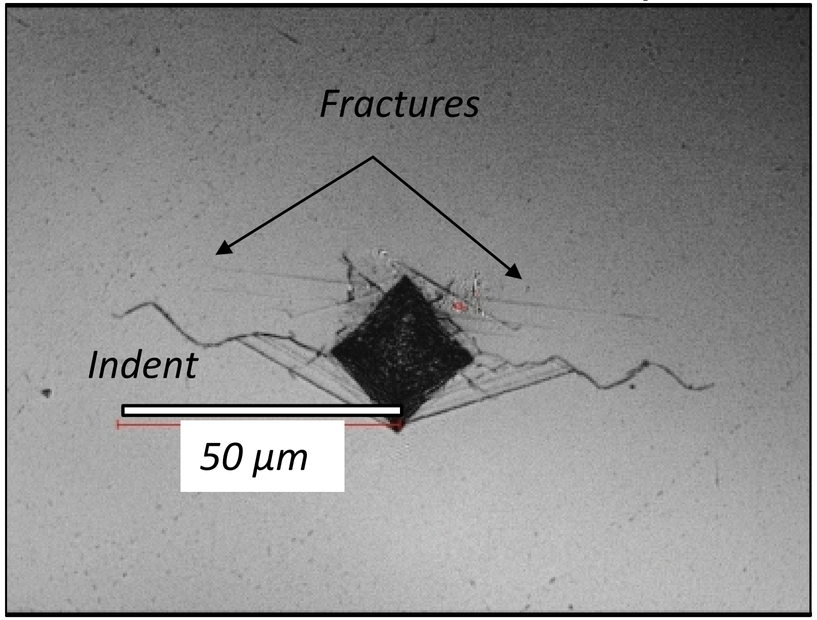


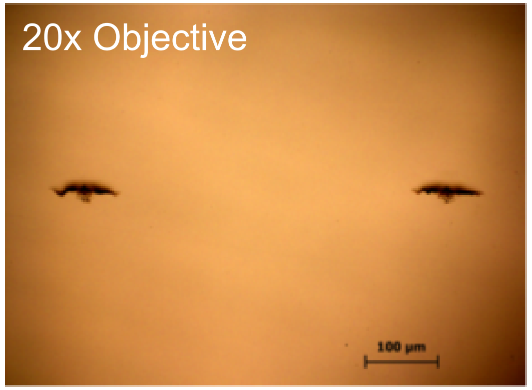


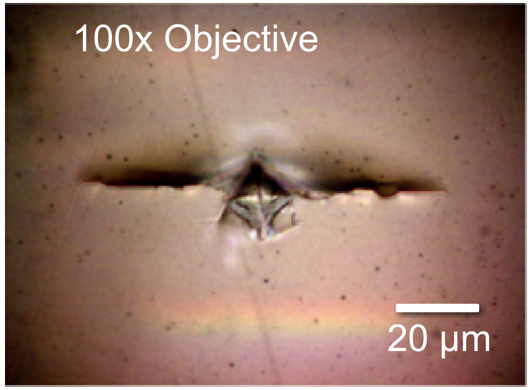
Part I: Chemical controls on subcritical fracture in calcite

Methods: nanoindentation and in situ crack growth

Calcite Indentation, Vickers tip, 400 mN







Vickers tip

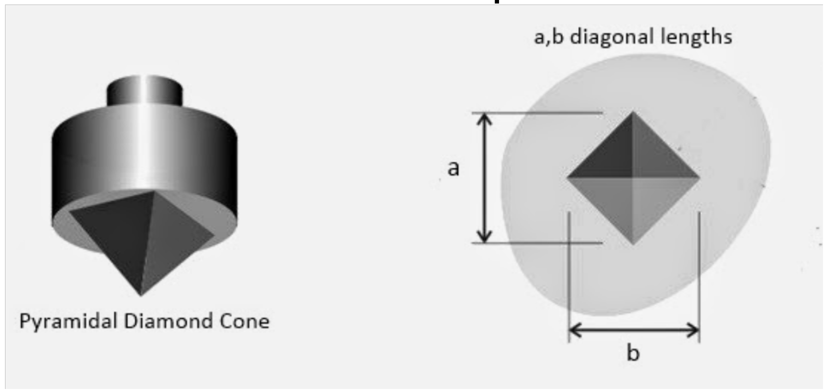
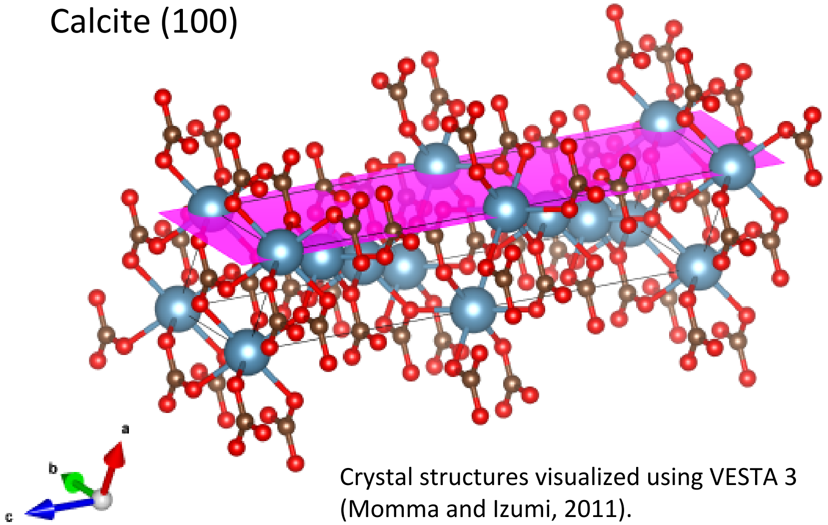


Image from: http://www.weldpedia.com/2014/10/macroscopic-and-microscopic-examination.html

Calcite (100)



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

Fracture toughness [1]:

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

[1] Lawn and Cook, 2012

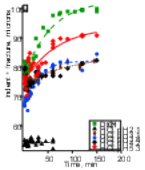
- Laboratory experiments to measure fracture propagation rate *in situ* as a function of chemical composition of the fluid;
- Single crystal calcite (100) indented using Vickers indenter tip at 400 mN force to induce cracking;
- Fractures are imaged *in situ* using optical microscope Nikon Eclipse 80i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

Ilgen, et al., 2018

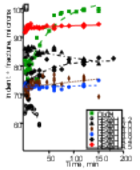
Scientific Reports, 8, 164656.

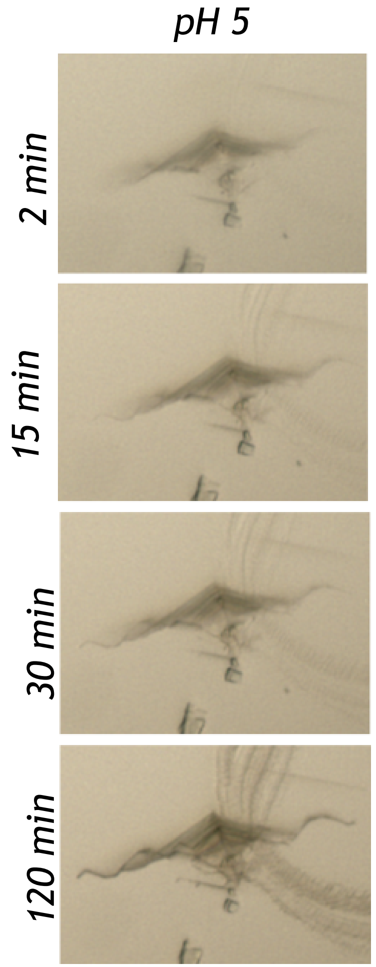
Results: fracture growth rate

HCl



H_2SO_4



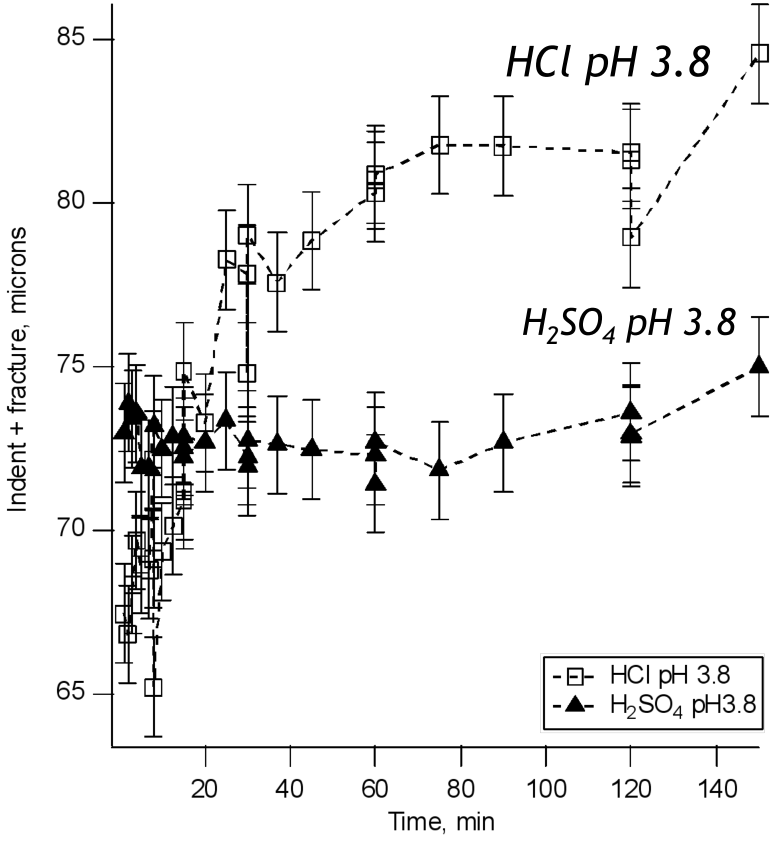


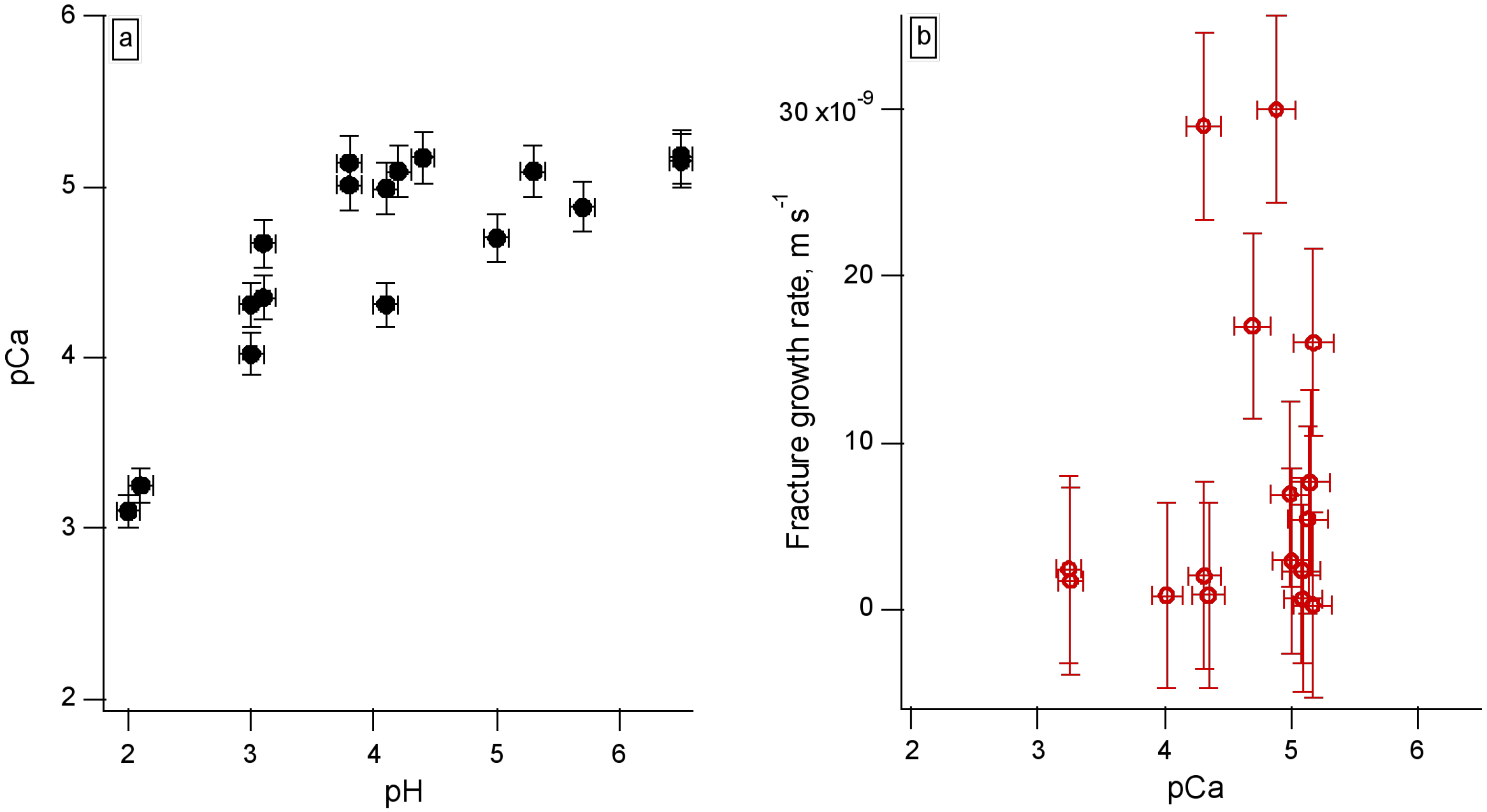
- The propagation rate of subcritical fracture measured *in situ* varied from 1.6×10^{-8} m s^{-1} to 2.4×10^{-10} m s^{-1}.

Ilgen, et al., 2018

Scientific Reports, 8, 164656.

Results: what controls crack growth?





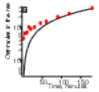
- Propagation rate of fracture in calcite is dependent on the anion.
- No correlation between the dissolution rate of calcite and subcritical fracture growth.
- Positive correlation between pCa and pH for all examined reactors; pCa = $-\log_{10}[Ca^{2+}]$;
- No correlation observed between pCa (proxy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

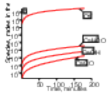
Ilgen, et al., 2018

Scientific Reports, 8, 164656.

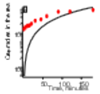
Results: what controls fracture growth?

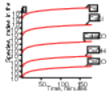
H_2O



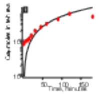


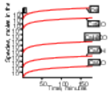
HCl





H_2SO_4



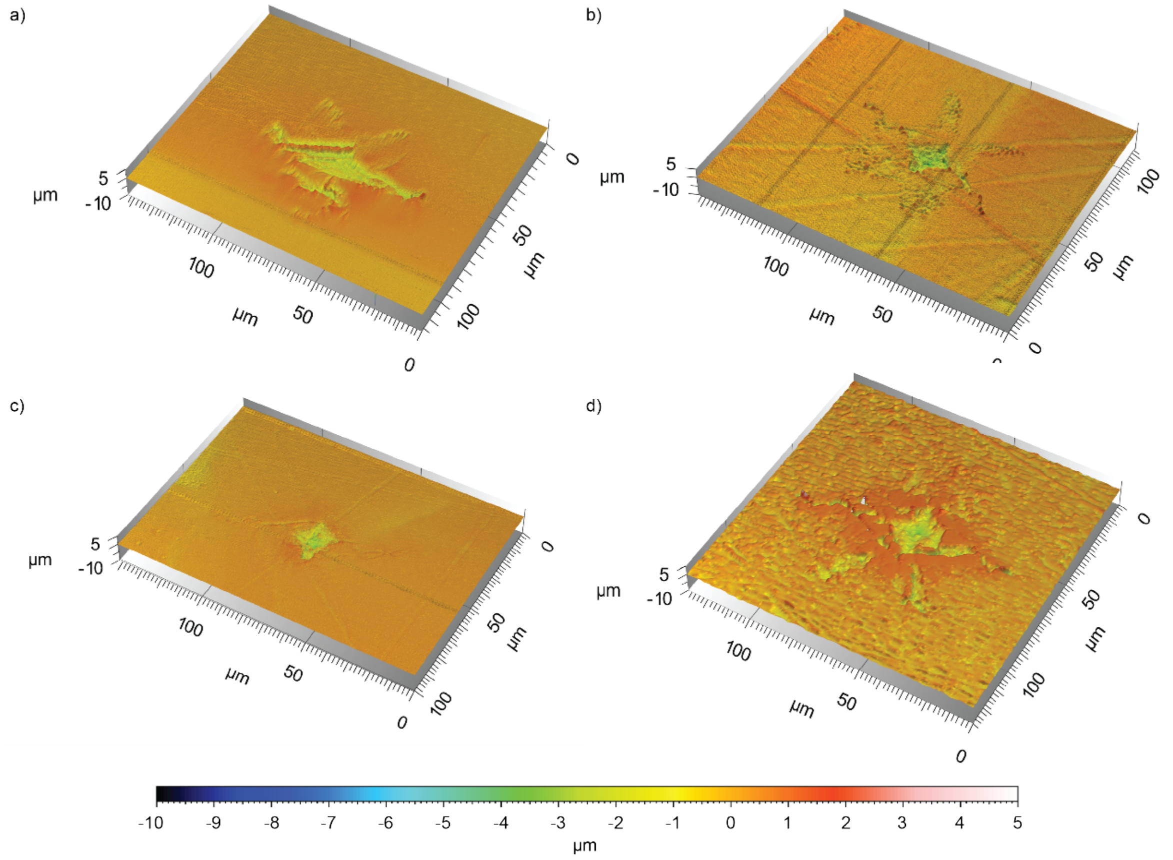


K_β for $CaCO_3$ is $10^{-7.128}$; K_β for $CaCl^+$ is $10^{0.7}$; and K_β for $CaSO_4$ is $10^{2.32}$

Ilgen, et al., 2018

Scientific Reports, 8, 164656.

Results: surface morphology and fracture toughness



(a) Sample exposed to H2SO4 at pH 2.0 for 150 minutes; (b) Sample exposed HCl at pH 3.8 for 120 minutes; (c) Sample exposed to fracking fluid at pH 4.1
for 180 minutes; and (d) Sample exposed to DI H2O for 1140 minutes.

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.

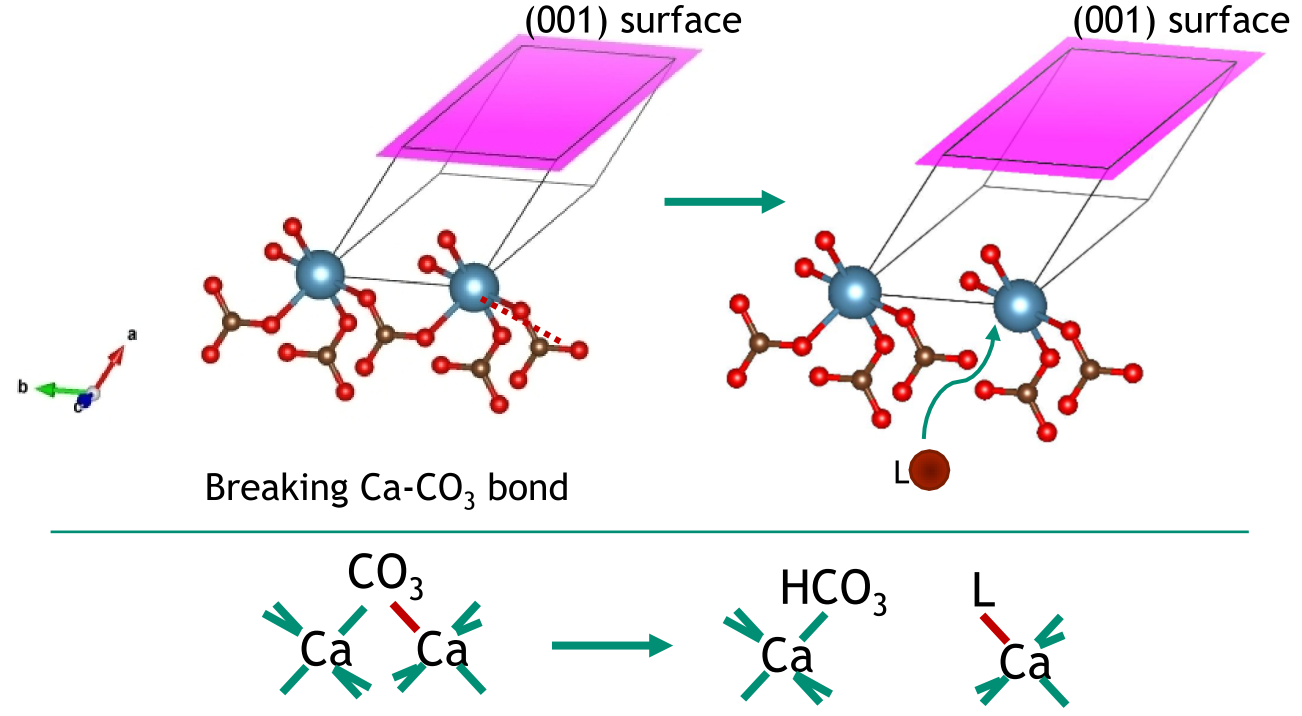
- The fracture width, measured on the surface of the sample, increased with decreasing pH, in agreement with enhanced calcite surface dissolution with decreasing pH.

Ilgen, et al., 2018

Scientific Reports, 8, 164656.

[1] Lawn and Cook, 2012

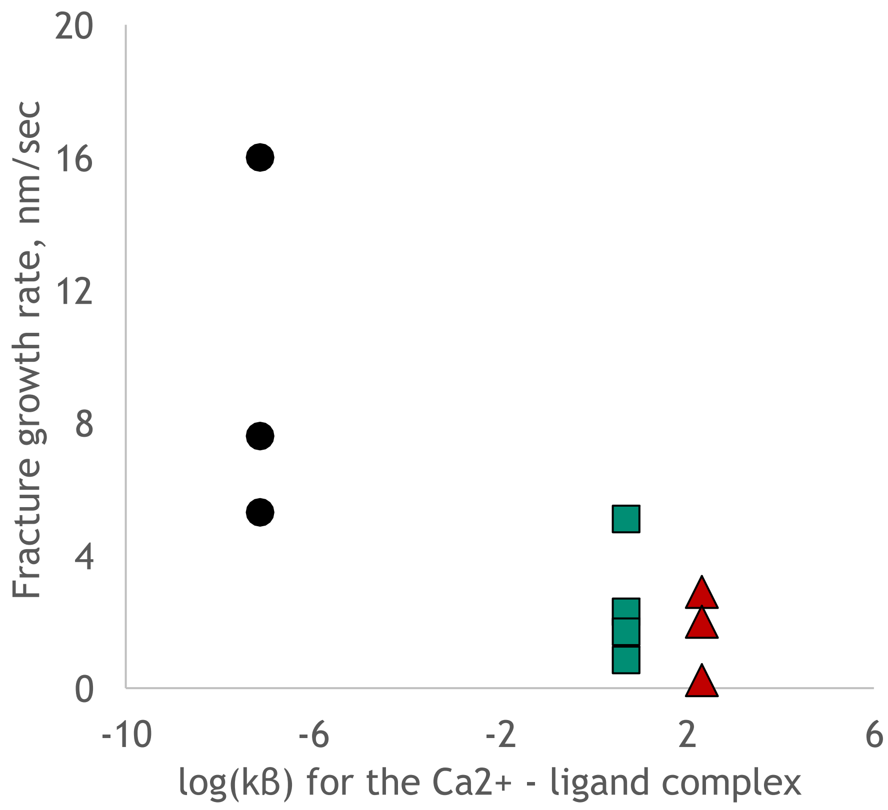
Results: Conceptual model



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

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

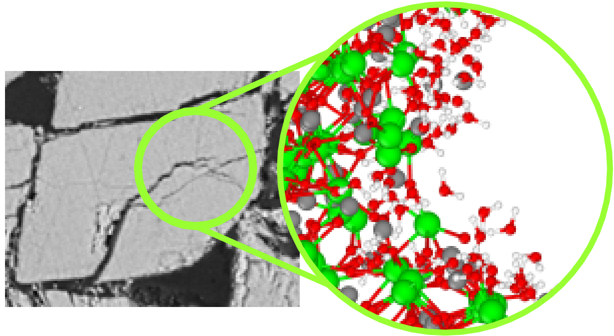
$>Ca—OH + H_2SO_4 \rightarrow >Ca—SO_4^- + H^+ + H_2O$



Ilgen, et al., 2018

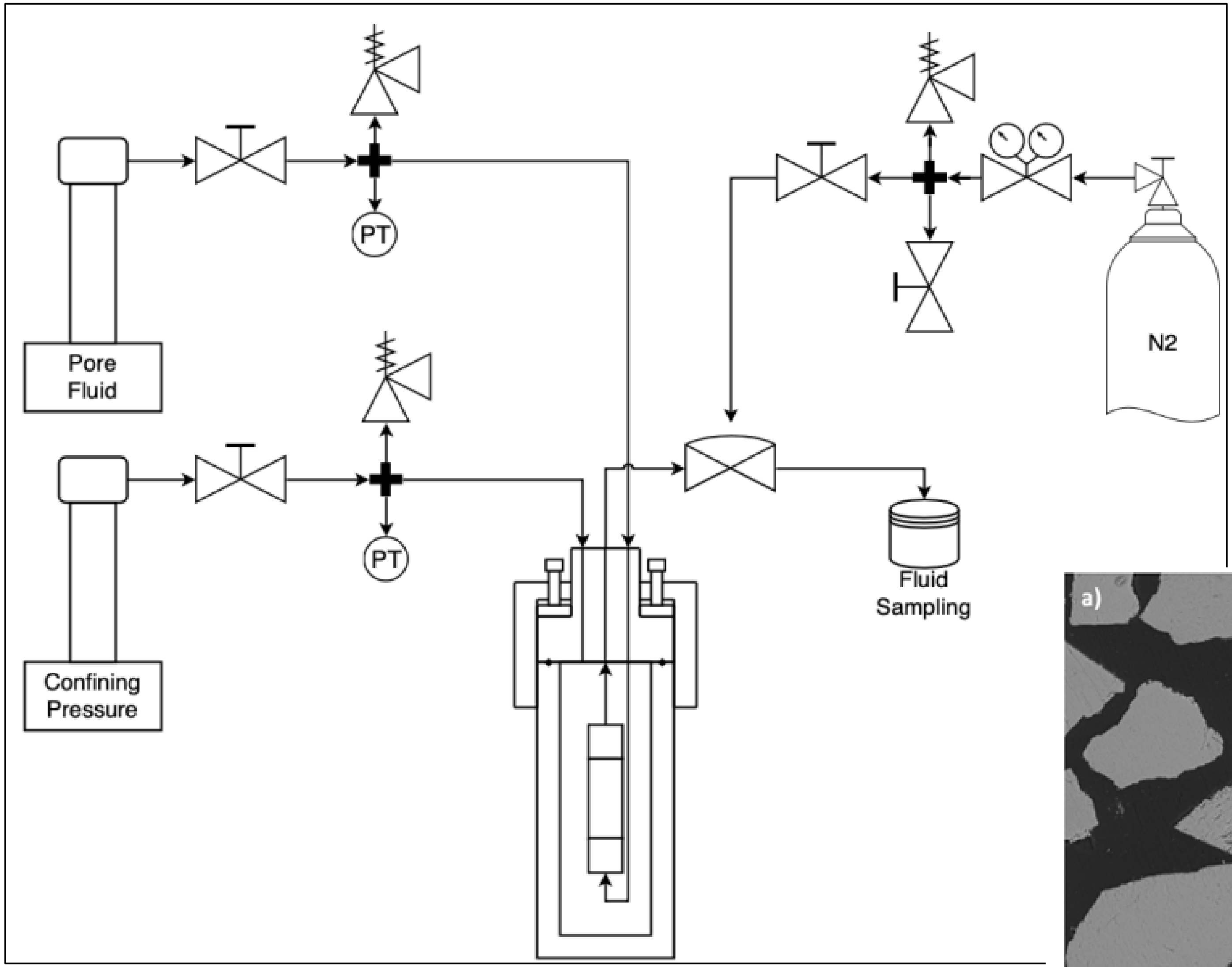
Scientific Reports, 8, 164656.

Part II: Strengthening of Calcite Assemblages through Chemical Complexation Reactions

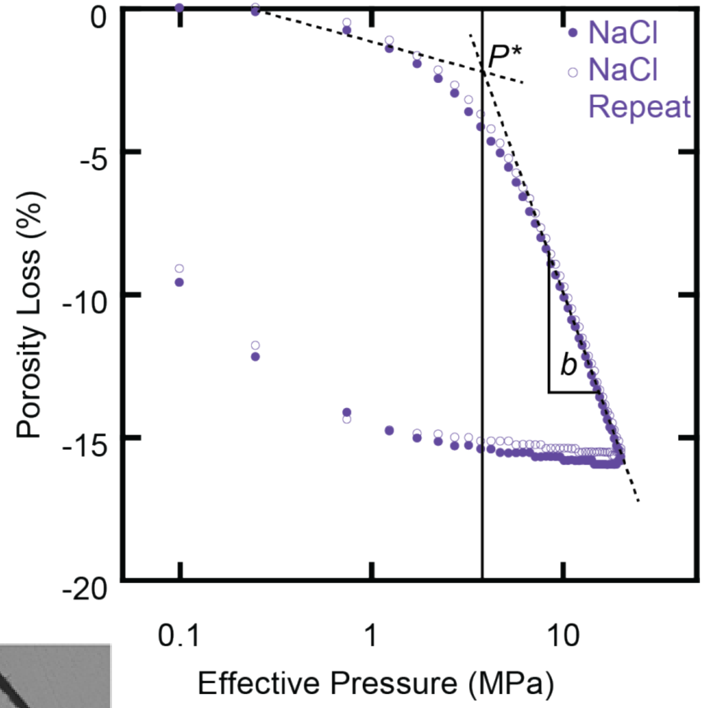


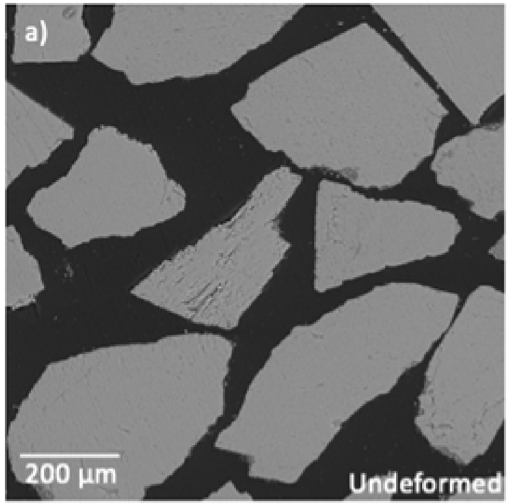
Experimental apparatus for consolidation tests

Schematic of consolidation apparatus



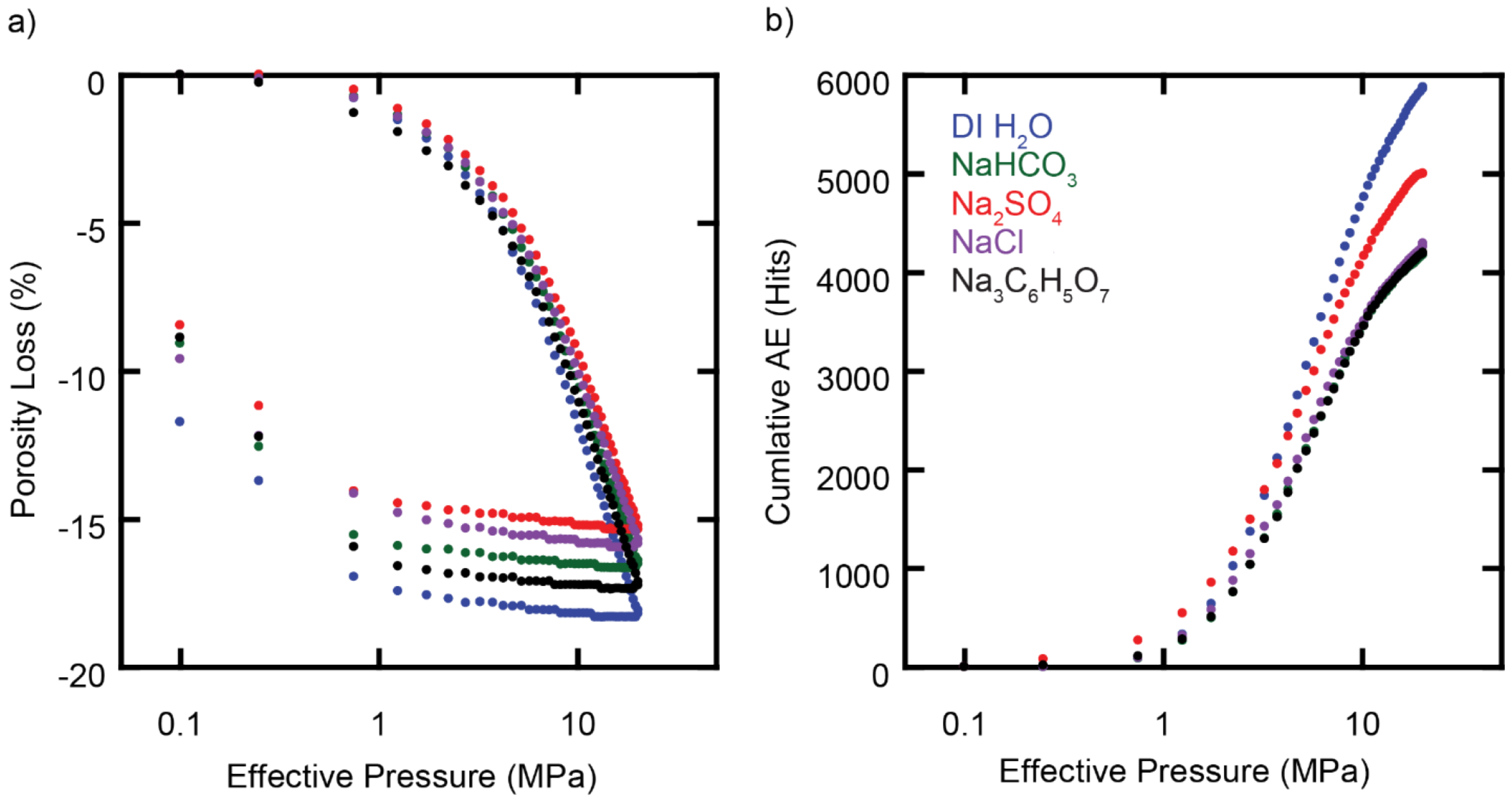
Consolidation curves





Starting calcite material, sieved to a grain size of 300-355 µm.

Results: porosity loss and acoustic emissions



a) Consolidation curves for granular calcite deformed with different interstitial pore fluids, showing porosity loss versus log effective pressure. b) Cumulative Acoustic Emissions (AE) during consolidation verses log effective pressure.

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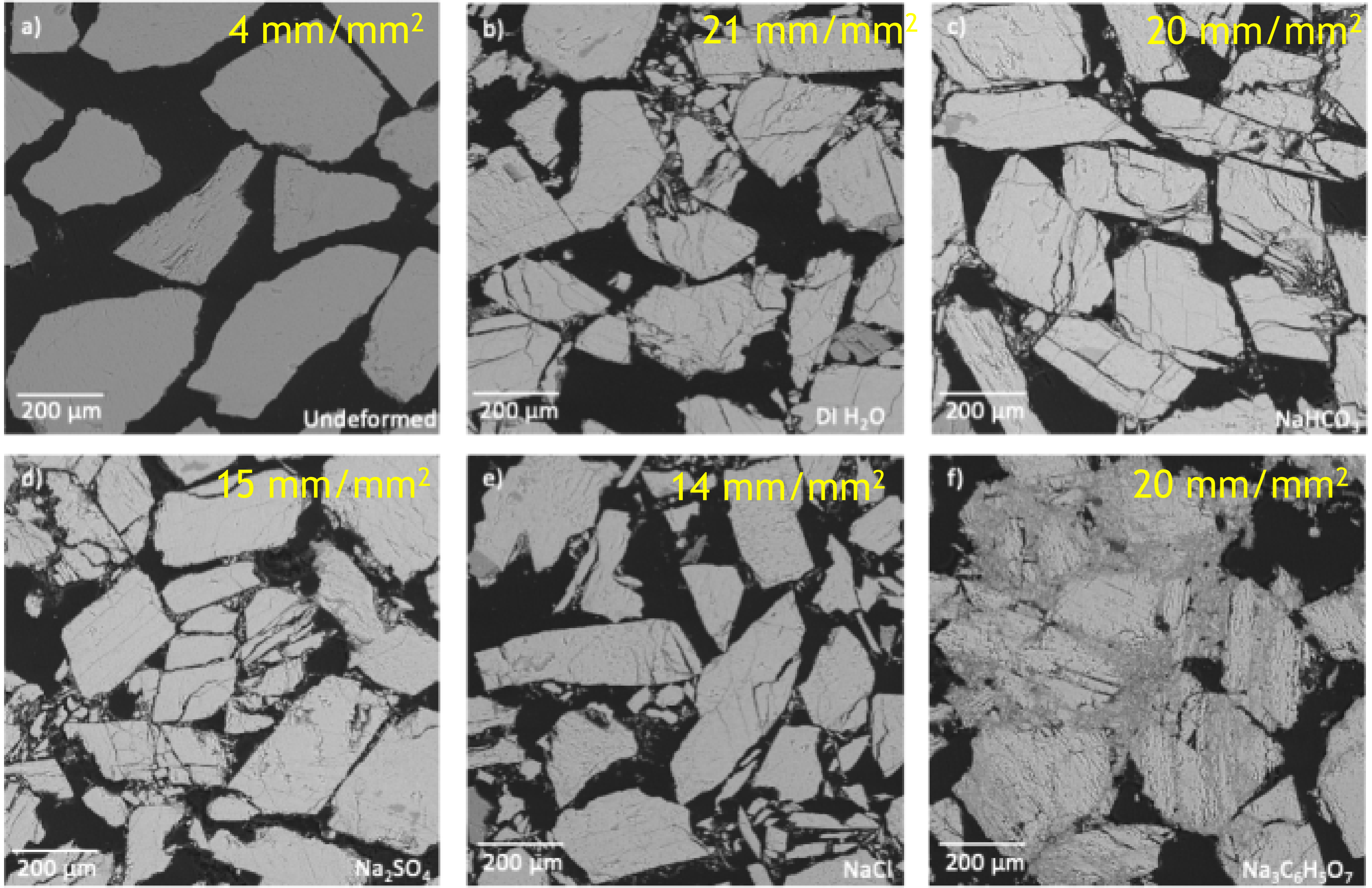
Results: microfracturing



- Scanning electron microscopy (SEM): a) Starting calcite material, sieved to a grain size of 300-355 µm.
- Samples consolidated in the presence of b) DI H_2O, c) $NaHCO_3$, d) Na_2SO_4, e) NaCl, and f) $Na_3C_6H_5O_7$.
- Fragmentation of grains and incorporation of crushed grains into interstitial pore spaces in all consolidated samples.
- $Na_3C_6H_5O_7$ diffusion is slower compared to other anions, it doesn't reach crack tip as it propagates.

Microfracture density depends on the fluid type and follows the sequence:
DI H_2O > $Na_3C_6H_5O_7$ > $NaHCO_3$ > Na_2SO_4 >NaCl

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Results: microfracturing

Table 1. Consolidation results for granular calcite.

Sample	P* (MPa)	Normalized P* by DI H_2O	Porosity Loss (%)	Consolidation Slope (%/MPa)	Total Microfracture Density (mm/mm^2)	% Grains affected by compaction	Modal Grain Siz (grain diameter in
Starting $CaCO_3$	--	--	--	--	3.5	0	325.0
DI H_2O	3.5	1	-18	20.5	21.1	71	29.0
$NaHCO_3$	3.65	1.04	19.3	19.3	19.9	80	28.0
Na_2SO_4	4.12	1.18	18.7	18.7	15.4	78	32.6
NaCl	3.90	1.11	18.6	18.6	13.5	75	28.2
NaCl Repeat	3.94	1.13	18.6	18.6	--	--	--
$Na_3C_6H_5O_7$	4.07	1.16	19.8	19.8	20.2	90	43.0

Microfracture density depends on the fluid type and follows the sequence:
DI H_2O > $Na_3C_6H_5O_7$ > $NaHCO_3$ > Na_2SO_4 >NaCl

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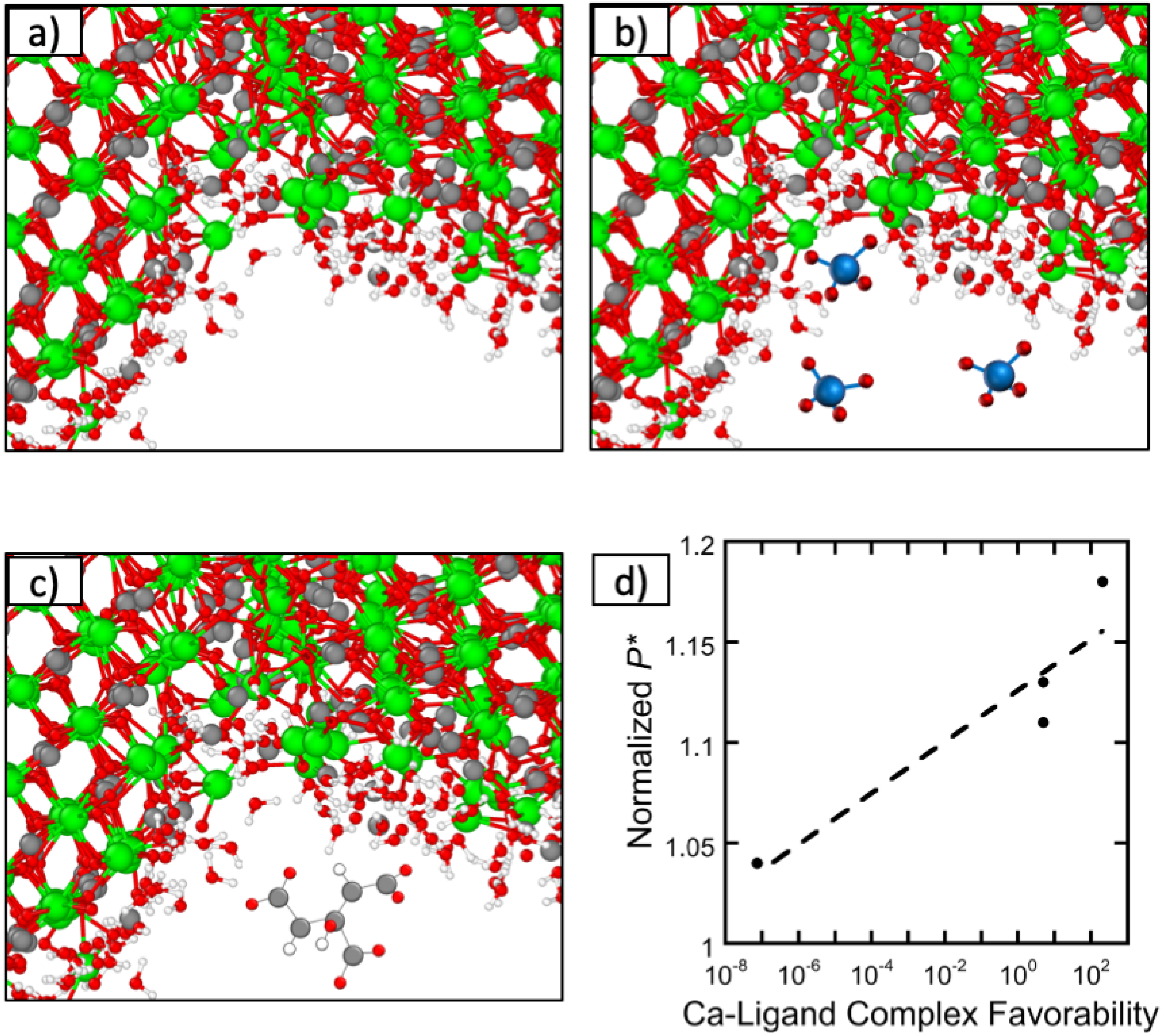
Results: Conceptual model



- Molecular-scale schematic of crack tip in calcite: red – oxygen, green – calcium, grey – carbon, blue – sulfur, white – hydrogen.

- (a) Calcite consolidation in de-ionized H_2O, with water hydrolyzing Ca−CO_3 bonds and promoting crack growth;
- (b) consolidation in 0.5M Na_2SO_4 with sulphate forming an Ca−SO_4 complex at the crack tip preventing hydrolysis reaction;
- (c) consolidation in 0.5M $Na_3C_6H_5O_7$ with citrate anion not reaching the crack tip before water does due to slower diffusion, compared to sulphate;
- (d) normalized P* versus Ca-anion complex favorability (K_β constant).

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Thank you.