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Chemical controls on granular compaction in calcite

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Introduction

Laboratory experiments were used to investigate chemical effects on brittle consolidation of granular calcite. Carbonates are common minerals in the shallow crust, forming framework grains and cementing phases for many sedimentary formations. Deformation of carbonates is likely to control the response of both porous reservoirs and impermeable caprocks, so the long-term success of resource extraction, waste disposal, and carbon sequestration will depend on the ability to understand and predict the chemical-mechanical response of carbonates to changing chemical environments.

Previous work has shown that subcritical crack growth in calcite is dependent on the chemical environment. In particular, recent work demonstrated that growth rates of fractures in nano-indented calcite are closely correlated to the type of aqueous ligand in brine solutions as opposed to pH or zeta-potential, suggesting that chemical complexation at the fracture tip controls growth rates. Here, hydrostatic consolidation experiments were conducted on saturated samples of granular calcite using similar ligands to upscale nano-indentation findings to geologically relevant assemblages.

We hypothesize that the chemical affinity between aqueous ligand and calcium in the calcite lattice controls in-situ fracture growth, and therefore compaction rate.

Previous Work

Ilgen et al., (2018) developed a novel way to investigate the effects of different fluid chemistries on fracture growth rate under subcritical stresses. 2mm x 2mm squares of single crystal calcite were indented using a Vicker's nanoindenter on the (100) crystal surface at forces of 400 mN. The calcite crystals were deformed dry and at room temperature. The loading process created an indent site with small scale fractures growing outward from the site and a zone of residual plastic stresses at the fracture tips. When submerged in a fluid bath, the chemical conditions changed at the fracture tip allowing the fractures to propagate. During exposure, growth rates were measured using an optical microscope, and post exposure, resulting fracture morphologies were measured using a white light LED surface profilometer. Calcite samples were exposed to 5 different fluids (DI H_2O, HCl, H_2SO_4, $H_2C_2O_4$, and a synthetic hydrofracturing fluid) with pH's ranging from 1.4 to 6.5.

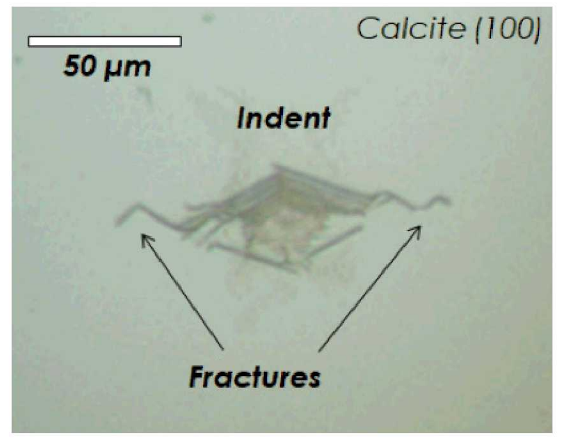


Figure 8a from Ilgen et al. (2018) showing the indentation site and the initial fractures. Initial size of fractures and indent ranged from 65-85 µm for all samples.

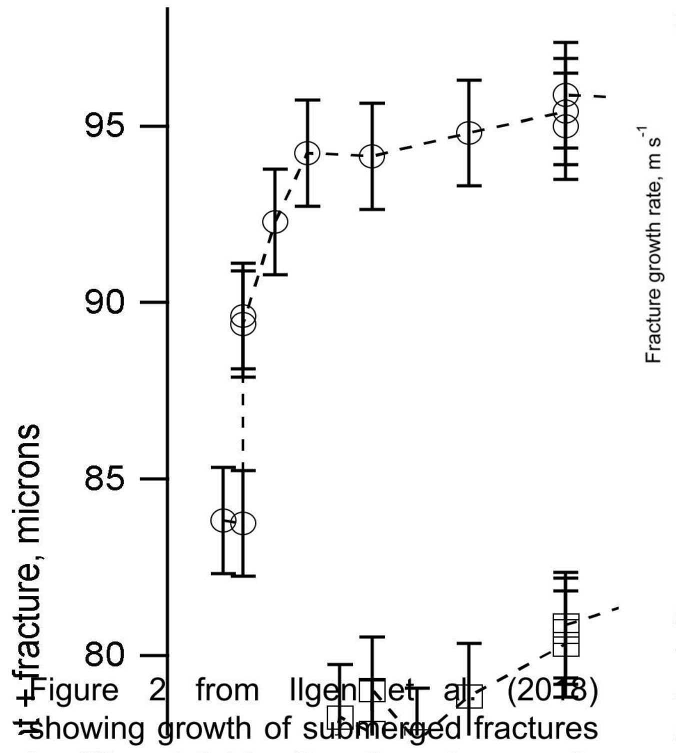


Figure 2 from Ilgen et al. (2018) showing growth of submerged fractures in different fluids. Growth varies greatly despite similar pH.

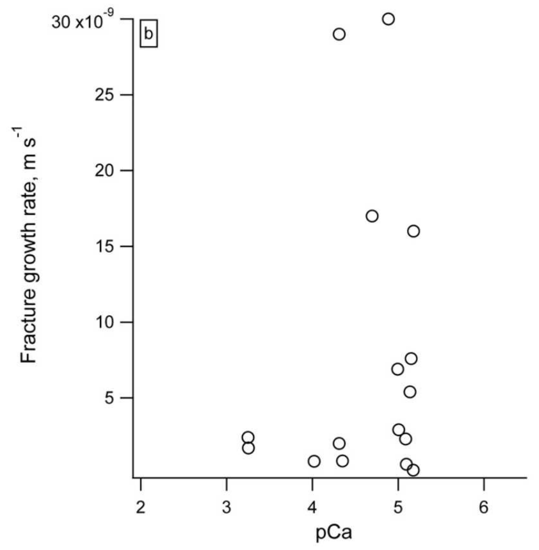


Figure 6b from Ilgen et al. (2018) showing the indentation site and the initial fractures prior to chemical exposure. Initial size of fractures and indent ranged from 65-85 µm for all samples.

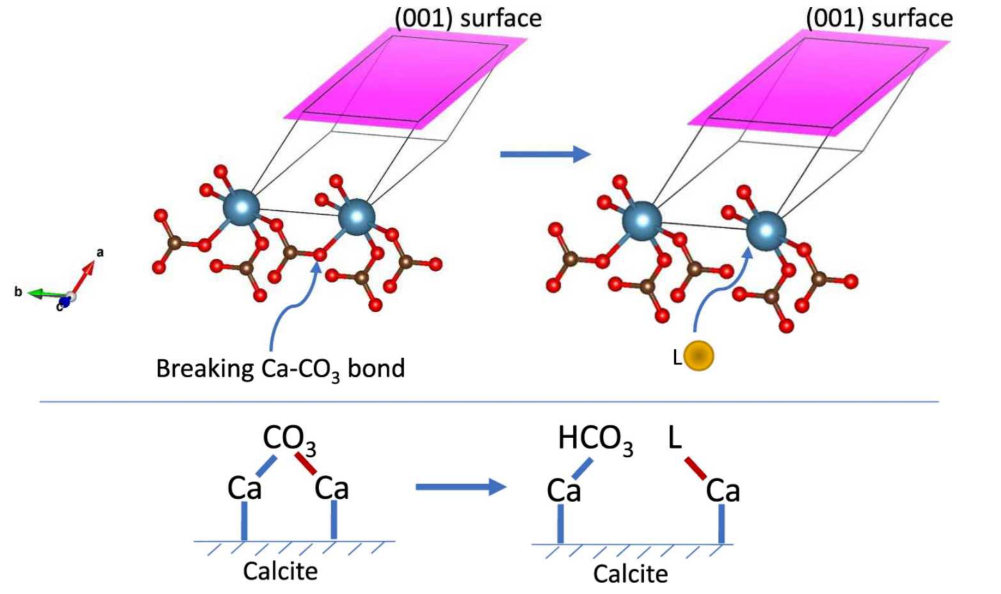


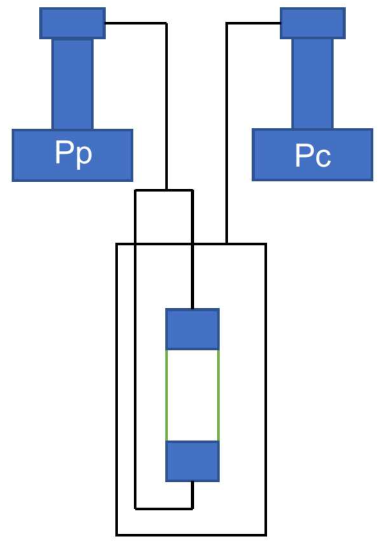
Figure 7 from Ilgen et al. (2018) showing the proposed model for chemical interaction at the crack tip. Subcritical fracturing is controlled by the chemical ligand's, L, ability to form complexes with calcite.

For CO_3^{2-} ligand: $>Ca—OH + H_2CO_3 \rightarrow >Ca—CO_3^- + H^+ + H_2O$
For Cl^- ligand: $>Ca—OH + HCl \rightarrow >Ca—Cl + H_2O$
For SO_4^{2-} ligand: $>Ca—OH + H_2SO_4 \rightarrow >Ca—SO_4^- + H^+ + H_2O$

Ilgen et al. (2018) found that decreasing pH values increased dissolution rates in calcite, but dissolution rates did not correlate with fracture growth. Neither did fracture growth rates correlate with surface charge or ξ-potential. Fracture propagation depended on the type of ligand present and its ability to form chemical complexes with Ca (K_β for $CaCO_3$ is $10^{-7.128}$; K_β for $CaCl^+$ is $10^{0.7}$; and K_β for $CaSO_4$ is $10^{2.32}$). The authors proposed a model where strongly complexing ligands essentially healed the fracture by forming complexes with surface Ca. These complexes shielded Ca-CO_3 bonds at the crack tip and prevented further rupture by disassociation with H_2O. By preventing H_2O from breaking bonds at the fracture tip, the fracture strength increased and the growth rate decreased.

To test this chemical mechanism, we performed hydrostatic consolidation experiments designed to induce extensive intragranular cracking in the presence of different ligands.

Methods

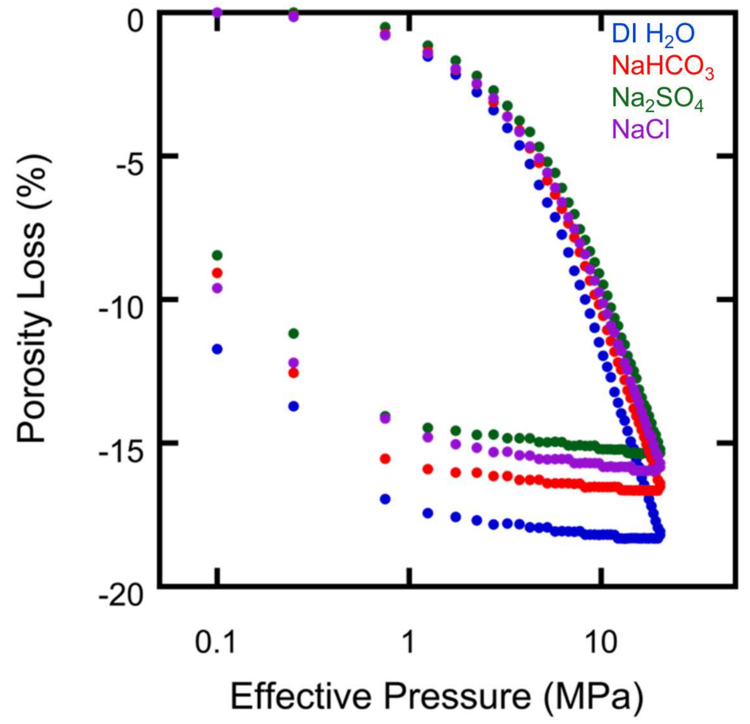


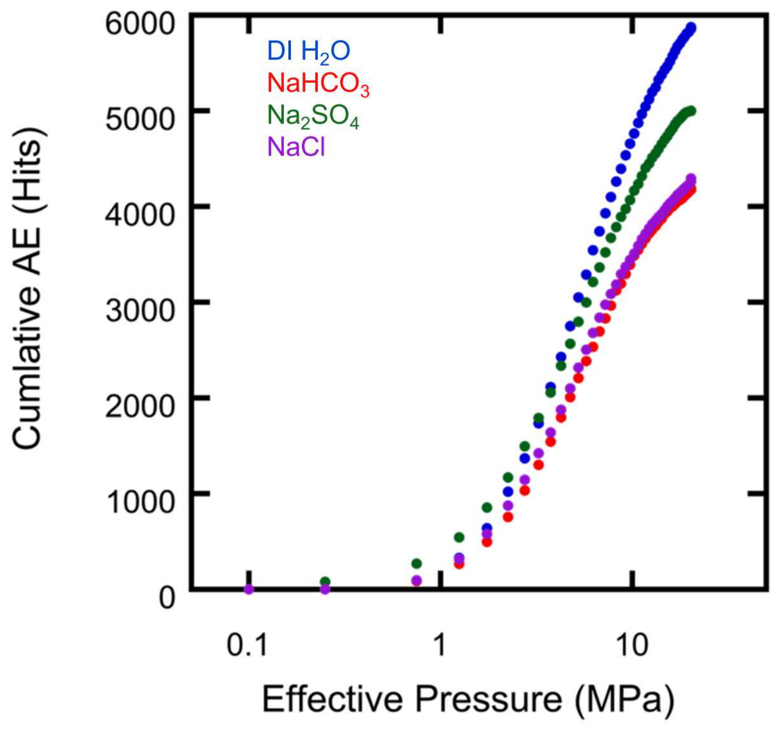
- Experiments were conducted on 99% natural granular calcite sieved to 300-355 µm
- Samples were prepared by pouring 30g of material into a preformed polyolefin jacket, 25mm diameter
    - Starting porosity 42±1% based on weight
- Samples were jacketed with an inner polyolefin jacket, a nickel foil jacket, and an outer polyolefin jacket
- Calcite was separated from the endcaps by Hastelloy frits
- Jackets were secured to the endcaps via 2 ni-chrome tie wires.
- Samples were saturated with 4 different pore fluid chemistries
    - DI H_2O,NaCl (pH 6.68), $NaHCO_3$(pH 8.12), Na_2SO_4 (pH 8.10)
- Samples were saturated in the vessel under a small confining pressure
- Samples were deformed through a hydrostatic consolidation load path
    - Hydrostatic pressure was increased by 0.5 MPa every 5 minutes to a maximum of 21.25 MPa.
    - Pore pressure was maintained at 1 MPa, and volume change was measured to calculate volume strain
    - Both ends of the sample were connected to an Hastelloy Isco pump for double ended drainage
    - The vessel was instrumented with a piezoelectric transducer to monitor acoustic emission, AE
- Post test, samples were prepared into thin sections
    - Grain size, fracture length, and fracture density were measured via SEM micrographs

Hydrostatic Consolidation

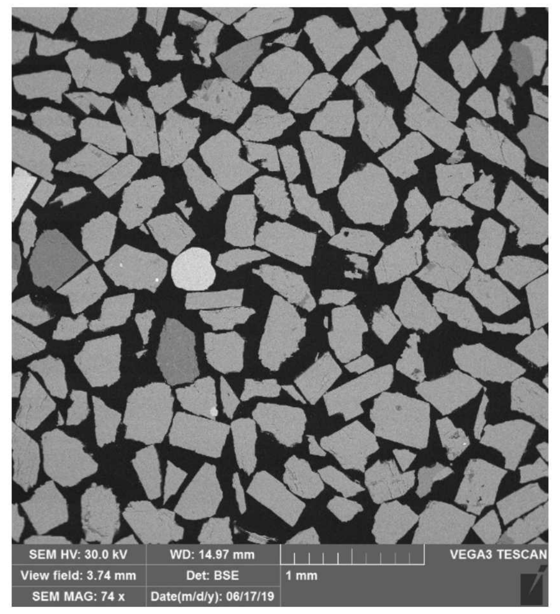
- Samples were consolidated to a maximum effective pressure of 20.25 MPa
- Similar shape to consolidation curve for all pore fluids
- Consolidation curve has two distinct regimes
    - Two different regimes corresponding to different micromechanisms
    - At low pressure, samples deform by grain rearrangement and rotation
    - At higher pressures, samples deform by grain cracking, pore collapse, grain comminution
    - Consolidation pressure, *P**, defines boundary
        - Picked based on change in slope (Choens and Chester, 2018, Karner et al., 2003)
- Increase in *P** with addition of brines compared to DI H_2O
- ~3%porosity loss difference at highest consolidation pressure between DI H_2O and Na_2SO_4
- Brines show less consolidation that DI H_2O
- Steep slope of consolidation curve fit with log relationship
    - Porosity loss=a+b*log(Effective Pressure)
    - b values similar, but differences between pore fluids
- DI H_2O has steepest compaction slope
- High levels of measured AE during consolidation
    - Indicates cracking
    - Possibly indicating 3 different behaviors
    - At highest pressures, grain cracking may be nearing completion
- DI H_2O has highest levels of measured AE which indicates highest frequency of fractures

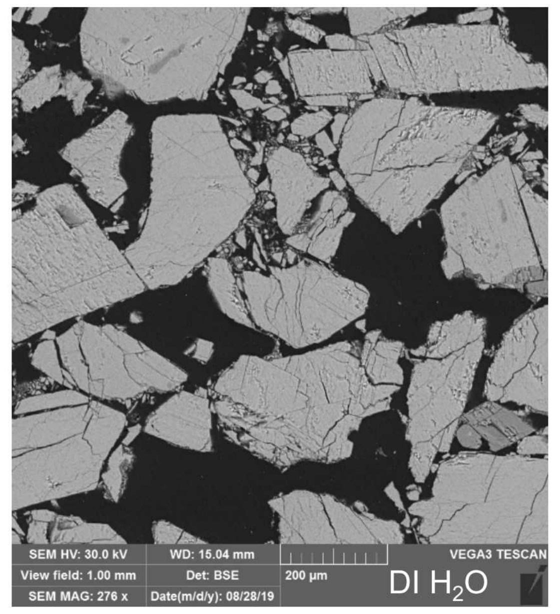
Sample	*P** (MPa)	Porosity Loss (%)	Compaction Slope (%/MPa)
DI H_2O	3.50	-18.2	-20.5
$NaHCO_3$	3.65	-16.5	-19.3
Na_2SO_4	4.12	-15.3	-18.7
NaCl	3.94	-15.8	-18.6



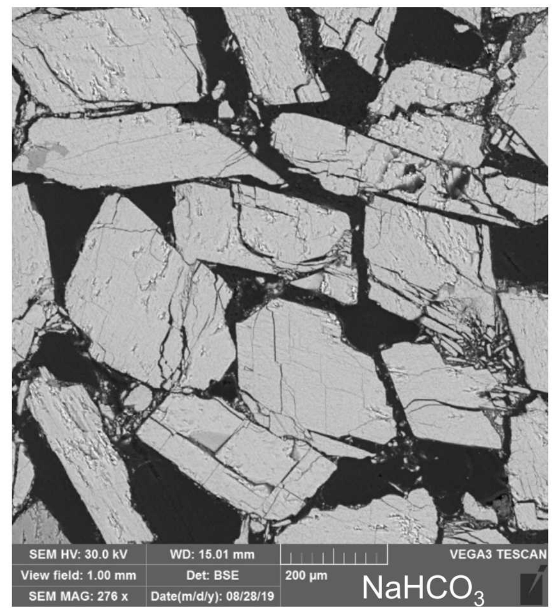


Microstructural Analysis

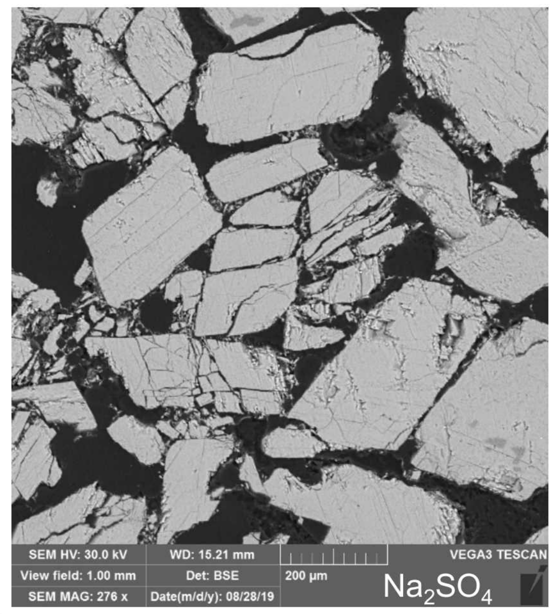




DI H_2O



$NaHCO_3$



Na_2SO_4

Sample	Cumulative Microfracture Density (mm/mm2)	Modal Grain Size (grain diameter in microns)
DI H_2O	18.5	29.0
Na_2SO_4	12.9	32.6
$NaHCO_3$	17.7	28.0
Uncompacted $CaCO_3$	nd	325

- SEM investigations show well sorted angular grains of calcite
- Post test, samples are highly fractured and reduced in grain size
    - Hertzian grain fracturing
    - No observed pressure solution or dissolution/precipitation
- Highest microfracture density in DI H_2O samples, lowest in Na_2SO_4 samples

Conclusions

- A series of hydrostatic consolidation experiments were performed on granular calcite packs in the presence of 4 different pore fluids
- Consolidation curves indicate multiple deformation mechanisms
    - Fracturing indicated by AE, confirmed by SEM observations
- Experiments show changes in behavior due to pore fluid chemistries
    - Small, but consistent through consolidation, AE, and microstructures
    - DI H_2O has highest porosity loss, lowest *P** value, steepest compaction slope, highest measured AE, and highest microcrack density
    - Na_2SO_4 has lowest porosity loss, highest *P** value, shallowest compaction slope, lower measured AE, and lowest microcrack density
- Consolidation behavior diverges around *P**
    - Differences in behavior due to chemical effects on fracturing
- Experimental hypothesis supported by results, see same relationship with pore fluids as Ilgen et al., 2018
    - Strengthening in brines compared to DI H_2O
    - Strengthening in SO_4 compared to Cl

Bibliography

Choens, R.C., and Chester, F.M. (2018). Time dependent consolidation in porous geomaterials at in situ conditions of temperature and pressure. *Journal of Geophysical Research: Solid Earth, 123.*

Croize, D., Bjørlykke, K., Jahren, J., Renard, F. (2010). Experimental mechanical and chemical compaction of carbonate sand. *Journal of Geophysical Research 115*(B11204).

Ilgen, A.G., Mook, W.M., Tigges, A.B., Choens, R.C., Artyushkova, K., and Jungjohann, K.L. (2018). Chemical controls on the propagation rate of fracture in calcite. *Scientific Reports 8*, 16465 doi:10.1038/s41598-018-34355-1.

Karner, S.L., Chester, F.M., Kronenberg, A.K., and Chester, J.S. (2003). Subcritical compaction and yielding of granular quartz sand. *Tectonophysics 377*(3-4), 357-381.

Rostom, F., Røyne, A., Dysthe, D. K. & Renard, F. (2013). Effect of fluid salinity on subcritical crack propagation in calcite. *Tectonophysics 583*, 68-75.

Røyne, A., Bisschop, J. & Dysthe, D. K. (2011). Experimental investigation of surface energy and subcritical crack growth in calcite. *Journal of Geophysical Research: Solid Earth 116.*

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