Surface Chemistry Controls on Crack Growth in Plagioclase Feldspars

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Introduction

Laboratory experiments were used to investigate the effects of interfacial reactions on elastic, plastic, and brittle properties of granular oligoclase. Plagioclase feldspars are principal components in crustal rocks as both crystalline and granular components. Utilization of subsurface reservoirs for water usage, energy production/storage, and carbon sequestration can modify in situ fluid chemistry within stressed crack tips at grain contacts. Combined with changes in pore pressure, fluid chemistry changes could lead to chemically-assisted cracks and result in enhanced damage to the reservoir system, altering hydrologic properties, storage capacity, and surface installations.

Previous work has shown that subcritical crack growth in calcite is dependent on the affinity of aqueous ligands to form surface complexes with Ca(II) in the crystal lattice. Here, in situ nanoindentation and hydrostatic consolidation experiments were conducted on saturated samples of granular oligoclase utilizing common environmental ions to to extend our findings to other calcium bearing geologically relevant minerals.

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

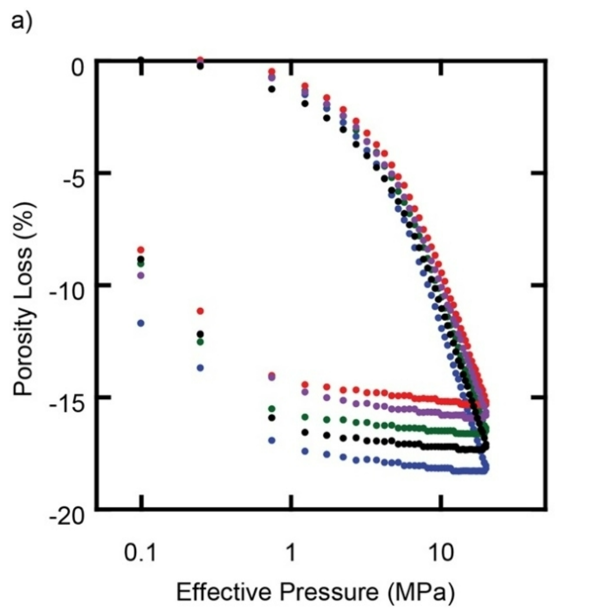
Previous Work

Ilgen et al., (2018) investigated the effects of various aqueous ligands on subcritical crack growth in calcite using a novel methodology of preloaded nanoindentation sites to create a zone of residual plastic stresses. When submerged in a fluid bath, the chemical conditions changed at the crack tip allowing the fractures to propagate. 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. Choens et al., (2021) followed up this study with hydrostatic consolidation of granular calcite in the presence of these same fluids at 0.5 M concentrations to upscale the previous findings to geologically relevant assemblages.

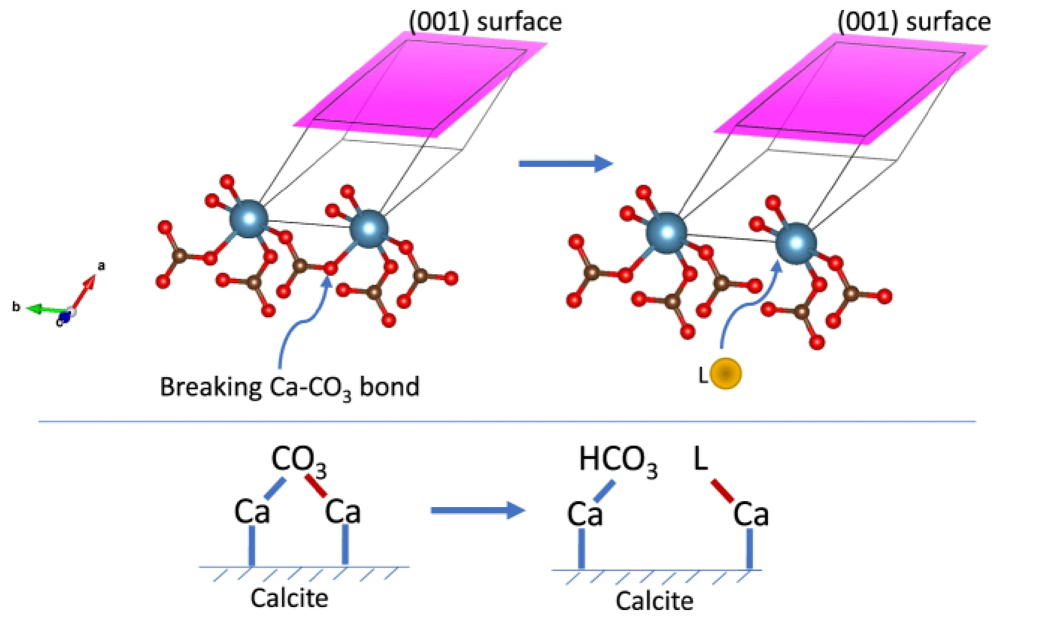
Both studies observed that crack growth and total induced fracturing depended on the fluid chemistry. Ilgen et al. (2018) found that decreasing pH values increased dissolution rates in calcite, but dissolution rates did not correlate with fracture growth. Neither did fracture growth rates correlate with 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 crack tip, the fracture strength increased and the growth rate decreased.

Choens et al., (2021) found that the presence of aqueous ligands hindered consolidation in comparison to DI H_2O, and strengthening effects increased with increasing complexation affinity, except when ligand size interfered with diffusion into the crack tip

Growth of submerged fractures varies greatly despite similar pH. (Figure 2 from Ilgen et al. (2018)).



Total consolidation of granular calcite depend on the aqueous ligand present in solution (Figure 1b from Choens et al. (2021)).

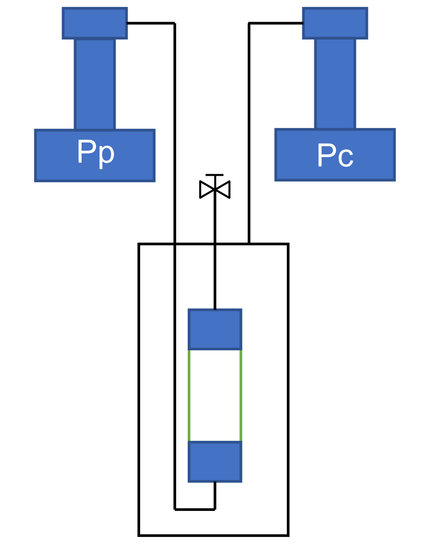


The conceptual model for chemical interaction at the crack tip shows subcritical fracturing is controlled by the chemical ligand's, L, ability to form complexes with calcite (Figure 7 from Ilgen et al. (2018)).

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

Methods

- Experiments were conducted on natural granular oligoclase sieved to 425-500 μm
- Samples were prepared by pouring 40g of oligoclase into a preformed polyolefin jacket with a 25mm diameter
  - Starting porosity 40±1% based on weight
- Samples were jacketed with two layers of heat shink polyolefin tubing, secured to titanium endcaps via 2 ni-chrome tie wires
- Oligoclase was separated from the endcaps by Hastelloy frits
- Samples were saturated with 3 different pore fluid chemistries at 0.5 M concentration
  - DI H_2O,NaCl (pH 6.68), and Na_2SO_4 (pH 8.10)
- Samples were deformed through a hydrostatic consolidation load path.
  - Hydrostatic pressure was increased to 51 MPa over the course of 12 hours
  - Pore pressure was maintained at 1 MPa, and volume change was measured to calculate volume strain
  - The vessel was instrumented with a piezoelectric transducer to monitor acoustic emission, AE
- Nanoindentation samples were prepared by potting sieved oligoclase grains in epoxy and preparing into polished 100 μm thin sections for nanoindentation. Each thin section was affixed to a 9 cm Pyrex dish using superglue
- Individual oligoclase grains were mapped using Hysitron TriboScan software. Each grain was initially indented under dry conditions at the maximum load of 1 mN. The unloading portion of the load-displacement curve was used to calculate reduced modulus and hardness of each grain
- Aqueous solutions (DI H_2O and Na_2SO_4) were added to the dish to cover the sample at ~ 3 mm depth. Then, nanoindentation of submerged samples was completed using the same method as for the dry surfaces

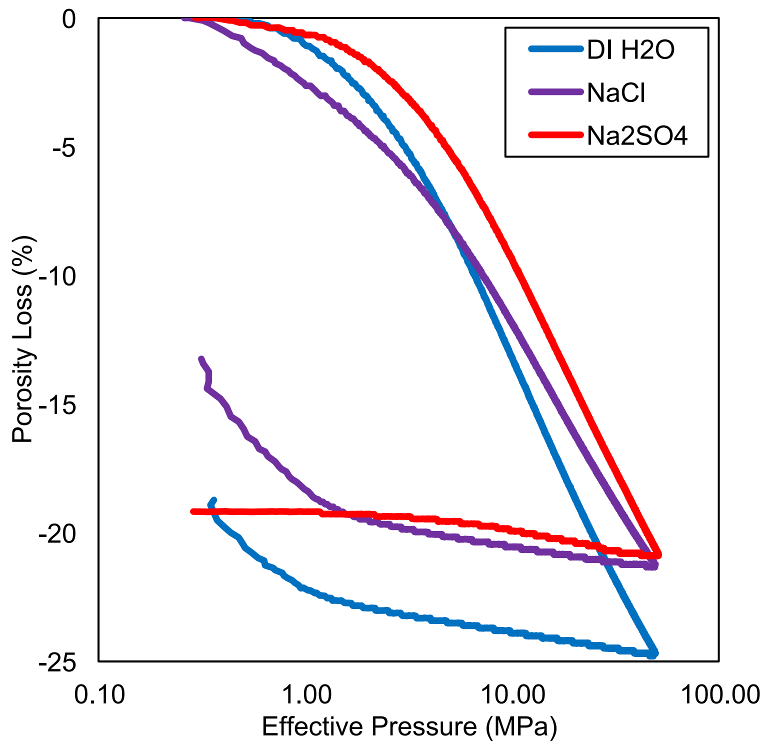


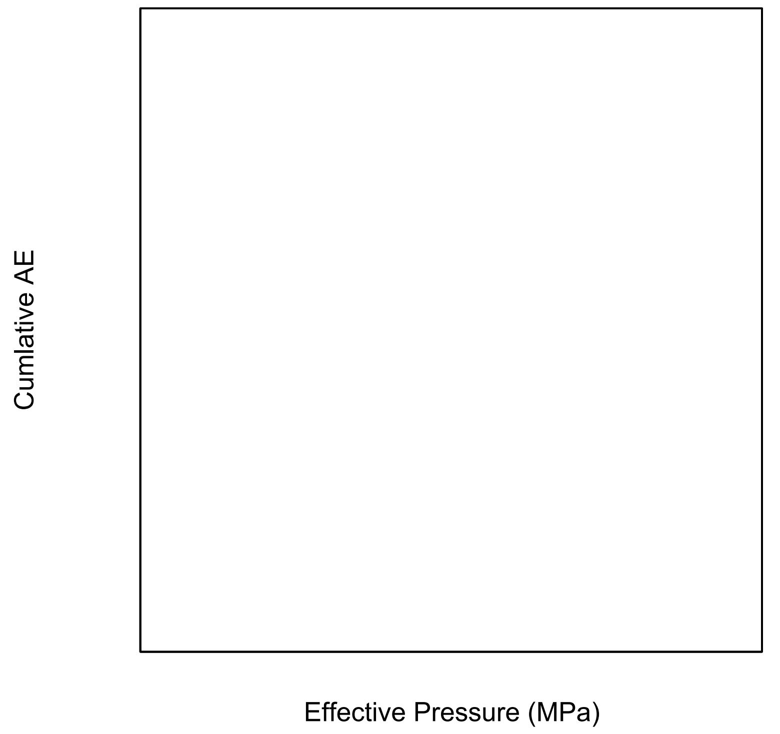
Consolidation setup: Independent confining and pore pressure syringe pumps. Pore fluid was flowed from bottom to top of sample under a small confining pressure and valved closed during testing for single ended drainage.

Hydrostatic Consolidation

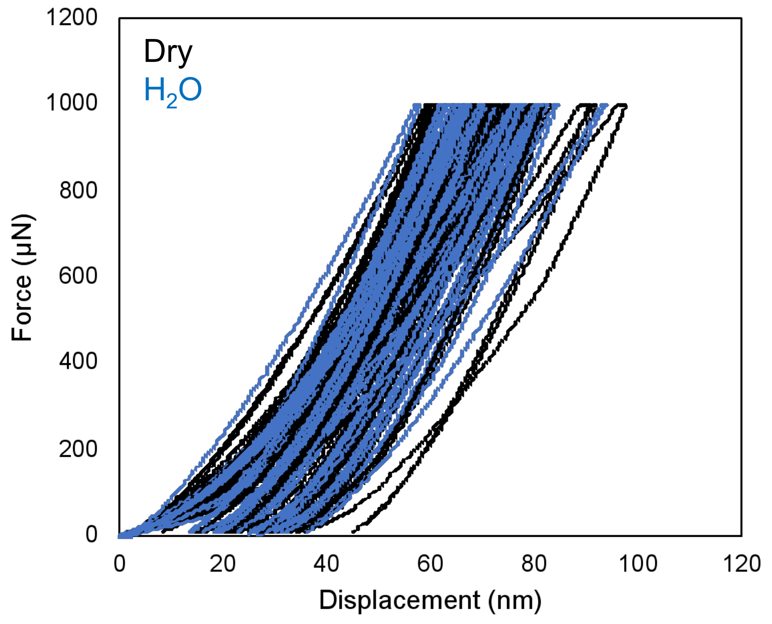
- Oligocase grain packs were consolidated to a maximum effective pressure of 50 MPa
- Similar shape to consolidation curves for samples saturated with DI H_2O and Na_2SO_4
  - Shallower for NaCl
- Consolidation curve has two distinct regimes
  - Two different regimes corresponding to different micromechanisms
  - 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 Na_2SO_4 compared to DI H_2O
  - NaCl has lowest P^* value
- ~4% porosity loss difference at highest consolidation pressure between DI H_2O and Na_2SO_4
- Brine saturated oligoclase shows less consolidation than DI H_2O saturated oligoclase
- Previous work demonstrated extensive intergranular fracturing resulting from similar consolidation experiments
- Steep portion 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, sliding
  - Error in recording pressure on AE system for NaCl
- AE higher in brine samples than DI H_2O, despite less overall compaction

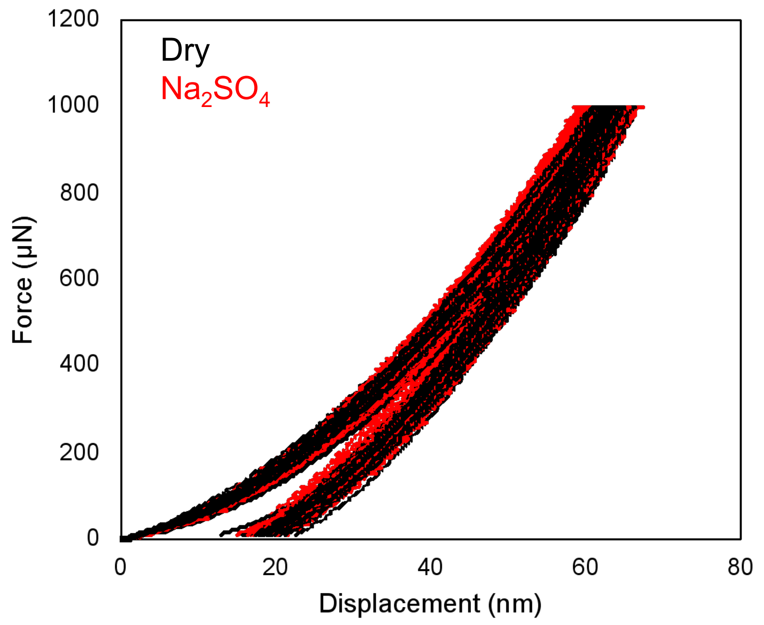
Sample	P^* (MPa)	Porosity Loss (%)	Compaction Slope (%/MPa)
DI H_2O	2.21	24.8	-7.4
Na_2SO_4	3.09	20.9	-7.0
NaCl	1.78	21.3	-5.9





Nanoindentation





Set 1	Contact Depth (nm)	Modulus (GPa)	Hardness (GPa)
Dry	46.5±5.3	88.3±10.0	10.5±1.6
DI H_2O	48.4±5.7	85.5±7.8	9.9±1.7

Set 2	Contact Depth (nm)	Modulus (GPa)	Hardness (GPa)
Dry	41.7±1.3	100.4±2.9	11.9±0.5
Na_2SO_4	40.2±1.8	100.8±3.8	12.5±0.7

- Comparisons of fluid effects of NaCl and Na_2SO_4 versus dry indented samples of oligoclase mounted in thin section
- 3-4 oligoclase grains were tested per fluid type
- Grains indented in DI H_2O see increases in contact depth, reduced moduli and hardness
- Grains indented in Na_2SO_4 see decrease in contact depth, increased moduli and hardness
- Results for fluid saturated oligoclase within standard deviation of dry measurement
- Results could be attributed to difficulty finding repeatable testing sites on thin section
  - Noticeably larger spread on Set 1 than Set 2
- Could also reflect that surface complexation affects subcritical crack growth, not elastic behavior

Conclusions

- A series of hydrostatic consolidation and nanoindentation experiments were performed on granular oligoclase packs in the presence of 4 different pore fluids
- Consolidation curves indicate multiple deformation mechanisms
  - Fracturing indicated by AE, previous work
- Experiments show differences in deformation of oligoclase due to pore fluid chemistries
  - Small, but consistent through consolidation
  - DI H_2O has highest porosity loss, lower P^* value, steepest compaction slope, lowest measured AE
  - NaCl has lower porosity loss, lowest P^* value, lowest compaction slope, highest measured AE
  - Na_2SO_4 has lowest porosity loss, highest P^* value, lower compaction slope, higher measured AE
- Consolidation behavior diverges around P^*
  - Differences in behavior due to chemical effects on fracturing
  - Odd behavior in NaCl saturated sample
- Consistent behavior for nanoindented oligoclase, but results not statistically significant
- Experimental hypothesis supported by results, see same relationship with pore fluids as Ilgen et al., 2018
  - Strengthening of oligoclase deformed in brines compared to DI H_2O
  - Strengthening of oligoclase deformed in the presence of SO_4 compared to Cl

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