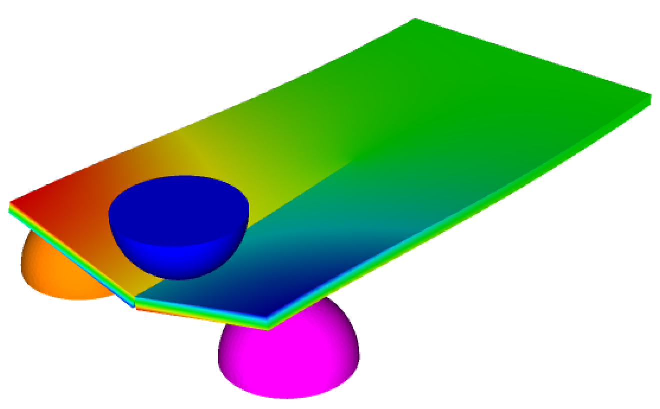
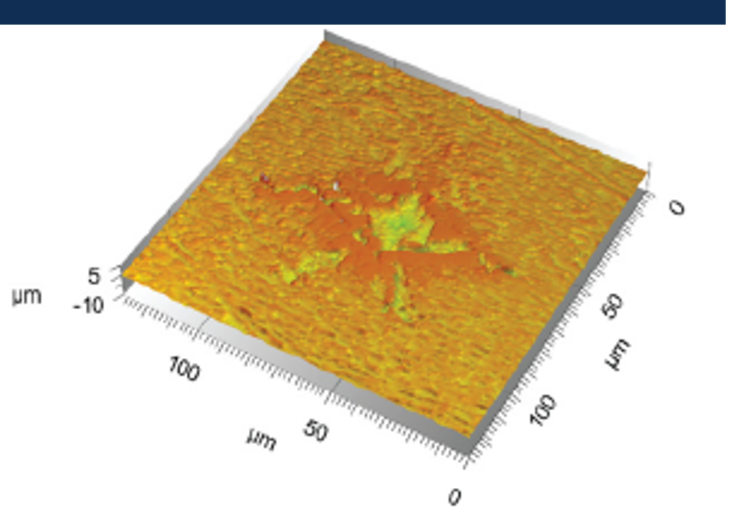
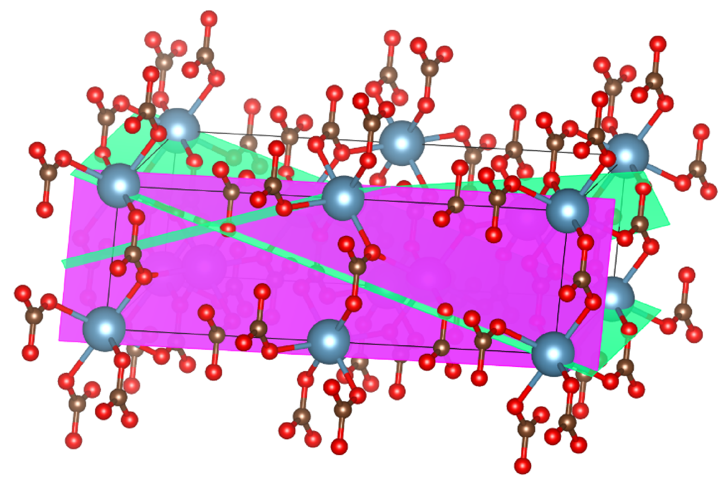
SAND2021-0380D

Chemical controls on the propagation and healing of subcritical fractures

PI: Anastasia G. Ilgen, PM: Hongyou Fan,
Scott Grutzik, Jessica Rimsza, and R. Charles Choens



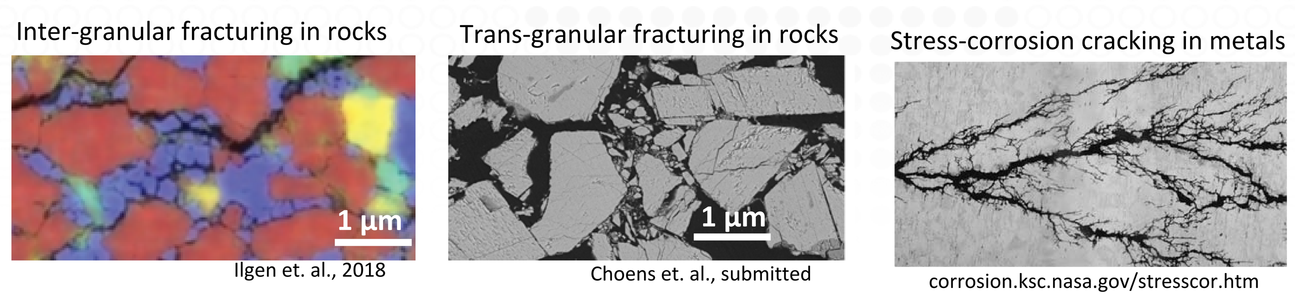




Problem

Chemically-assisted fracturing in crystalline materials

Subcritical, or, chemically-assisted, fracture controls deformation and permeability of rocks, and degradation of manmade materials. Chemical reactions at individual crack tips can lower effective fracture toughness for crystalline phases making up sedimentary rocks, concretes, and ceramics. Chemical effects on crack propagation have been recognized for several decades, and yet chemical mechanisms involved in subcritical fracture are still debated.[1-3]



Objective

Science Question and Hypothesis

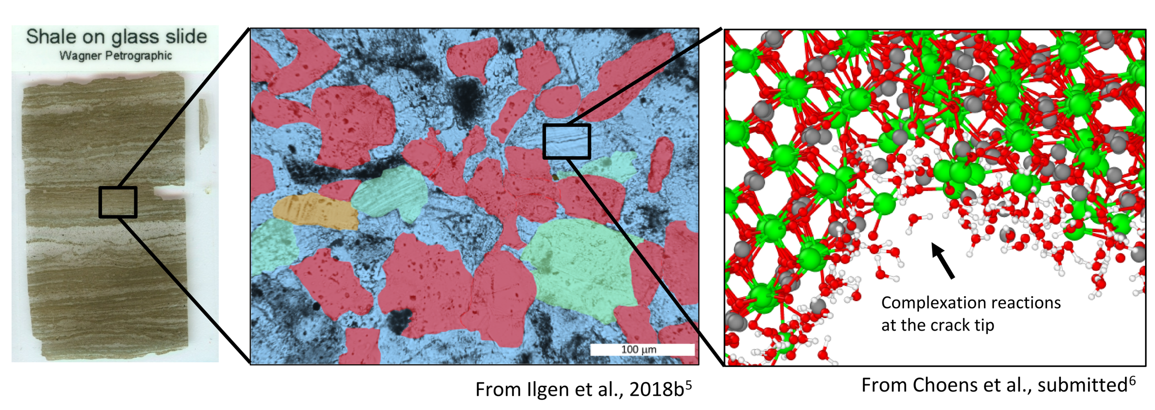
This proposed research is based on our earlier unexpected discovery: we found that chemical complexation reactions at the crack tip in calcite change effective fracture toughness *in situ*. By changing the chemistry of the liquid in contact with calcite we can either promote crack growth by adding weakly-binding ligand or arrest it by adding a strongly-binding one.[4] This newly discovered chemical mechanism needs further validation, in particular we propose to determine whether it applies to other crystalline phases, and how it manifests under mechanical loading.

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, due to the corresponding increase in effective fracture toughness.

Approach

Multi-scale investigation of chemically-assisted fracturing

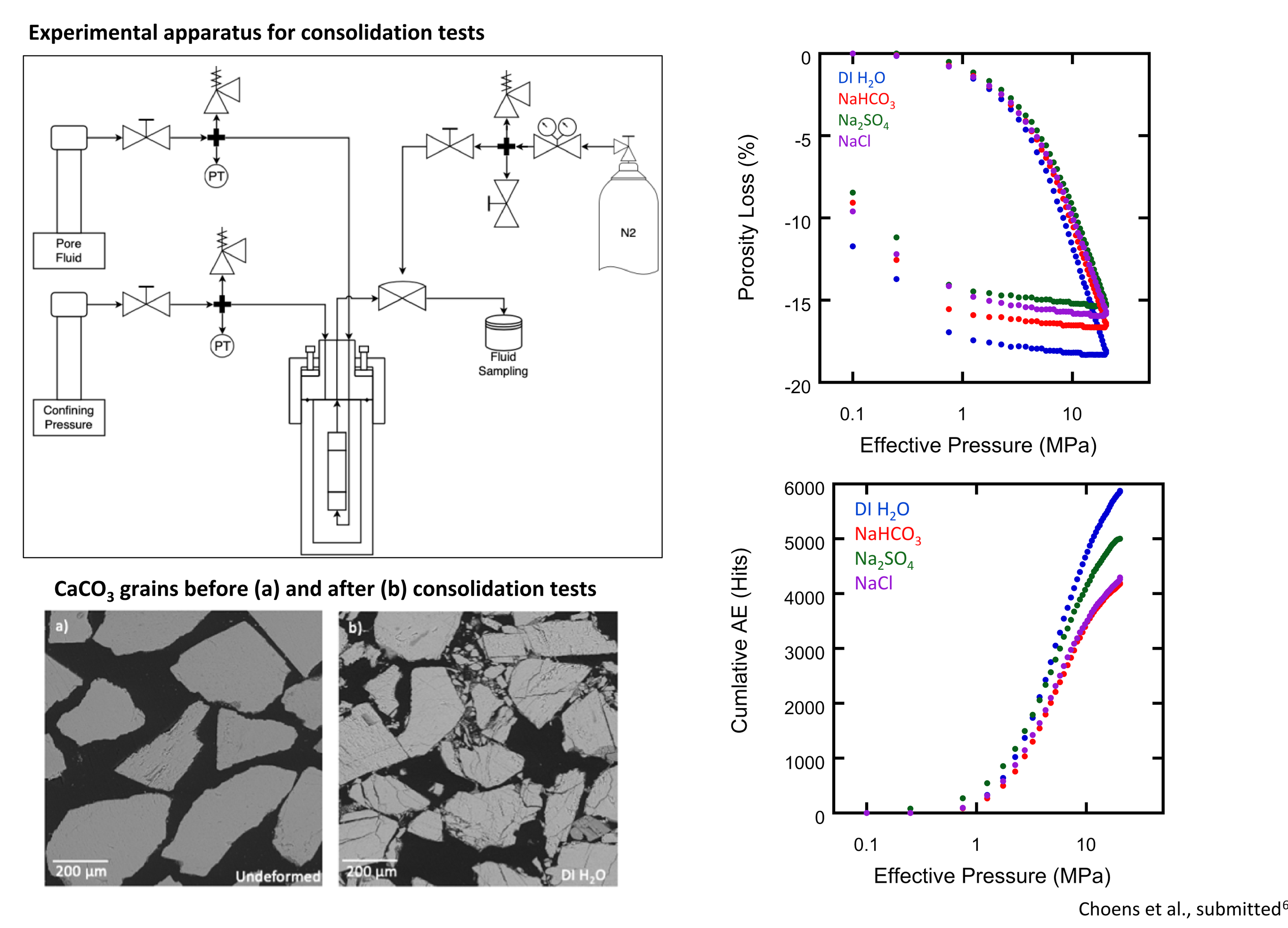


Griffith theory: $\boldsymbol{U = (U_E - W_L) + U_S}$, where U is the internal energy of the system, U_E is the elastic potential energy, W_L is the external work, and U_S is the energy from the added surface area of the crack.[7]

- The subcritical chemically-assisted fracturing = breaking chemical bonds at an atomically-sharp crack tip.[8]
- The coupled chemical-mechanical processes at individual crack tips manifest to the macroscopic scales.[9-11]

Planned Experiments and Modeling

- **Nano- and micro-mechanical testing** of single crystal $CaCO_3$, CaO, SiO_2, and CeO_2 in dry conditions and in aqueous fluids: *quantifying effective fracture toughness, local hardness and Young's Modulus in chemical environment.*
- **Vibrational spectroscopy testing** on pre-cracked crystals: *characterize strain near indent site and around cracks.*
- **Consolidation testing** of poly-crystalline packs in aqueous fluids with varying chemistry: *quantifying onset of fracturing, fracture density and geometry in pressure conditions and chemical environments relevant to subsurface reservoirs.*
- **Reactive Molecular Dynamics Simulations** of CaO Fracturing: *identifying chemical mechanisms and elementary reaction steps during crack growth*.
- **Finite Element Modeling of single cracks with chemistry** of fracturing in chemically-reactive environments: *Continuum finite element models of Double Torsion (DT) and indentation experiments are used to compute crack driving forces. Crack propagation can be modeled using crack growth laws fit to measured crack velocity data.*



Continuum modeling of compaction experiments

- We plan to use an existing continuum sintering model in SierraMechanics[15] to simulate compaction experiments.
- Dimensional analysis is used to relate sintering model parameters to crack growth laws fit to data from DT and indentation experiments

Macro-scale sintering law

$$\dot{\epsilon}^{in} = \alpha\sigma\left(\frac{\rho}{\rho_D}\right)^{\beta}\left(1-\frac{\rho}{\rho_D}\right)^{\gamma}$$

Micro-scale crack growth law

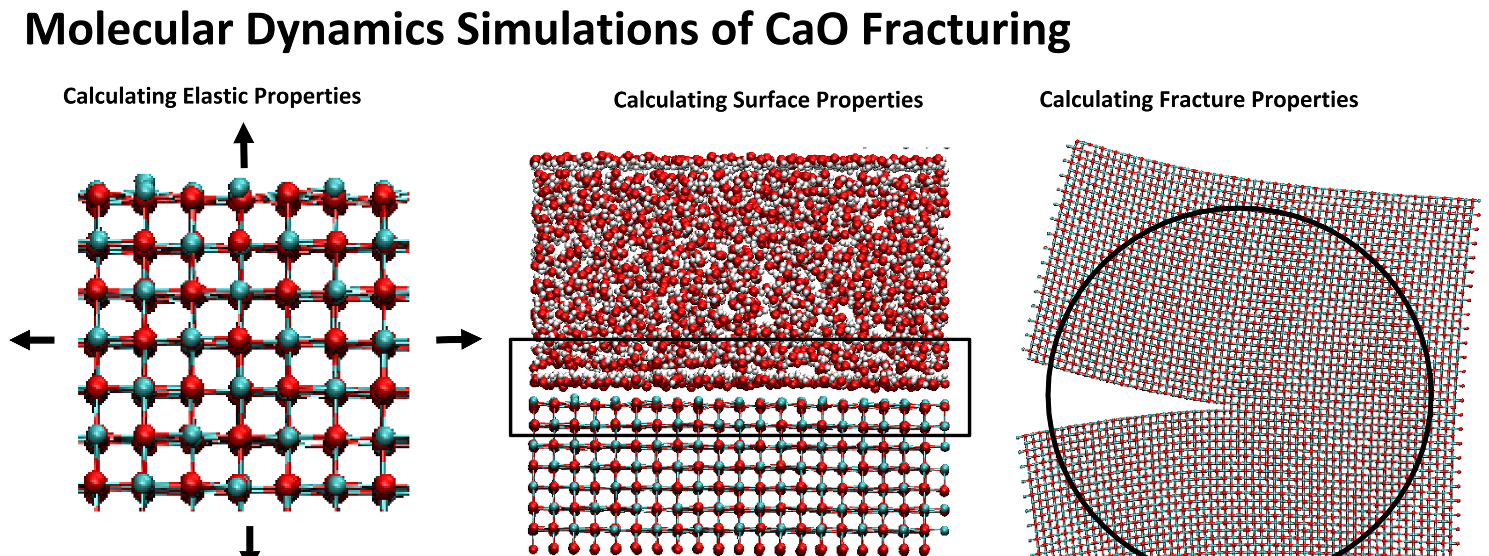
$$\dot{a} = A\left(K_I/K_{Ic}\right)^{b}$$

Sintering law informed by crack growth data

$$\dot{\epsilon}^{in} = \frac{Y^{b+2}A\eta\rho_c K_{Ic}^2}{E\sigma}\left(1-\frac{\rho}{\rho_D}\right)^{b/2+1}$$

Results

Molecular Dynamics Simulations of CaO Fracturing

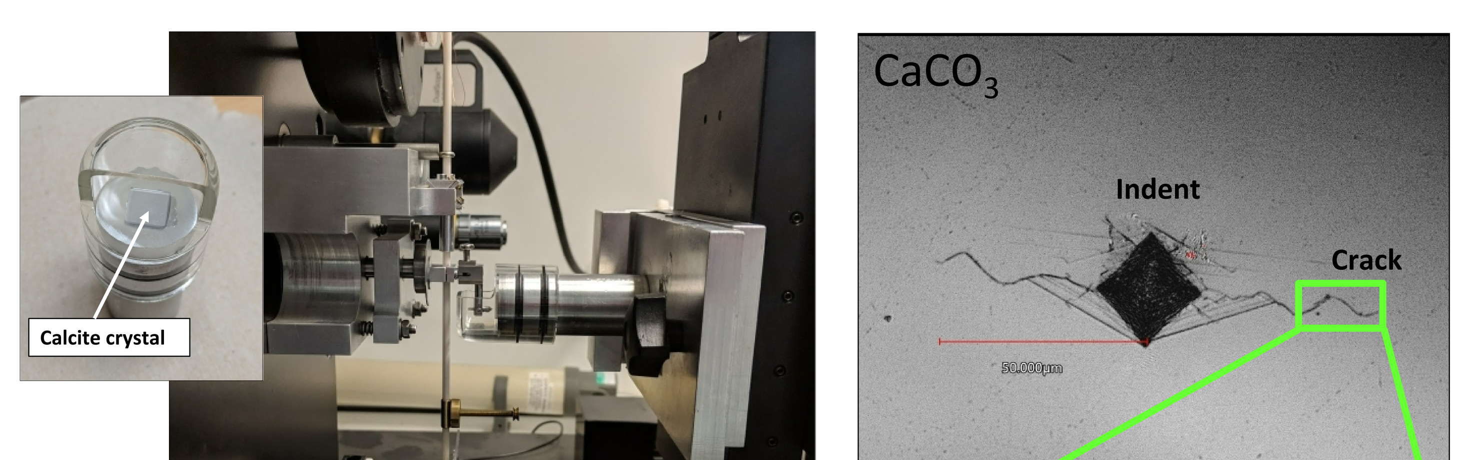


Property	Our Work	ReaxFF (Manzano et al.)[12]	Experiment (Speziale et al.)[13]
Density (g/cm^3)	3.33	-	3.34
Young's Modulus (GPa)	226.3	221.2	219.4
Bulk Modulus (GPa)	104.1	101.2	112.0
Shear Modulus (GPa)	91.7	84	80.5
Surface Energy (J/m^2)	0.67	0.73	-

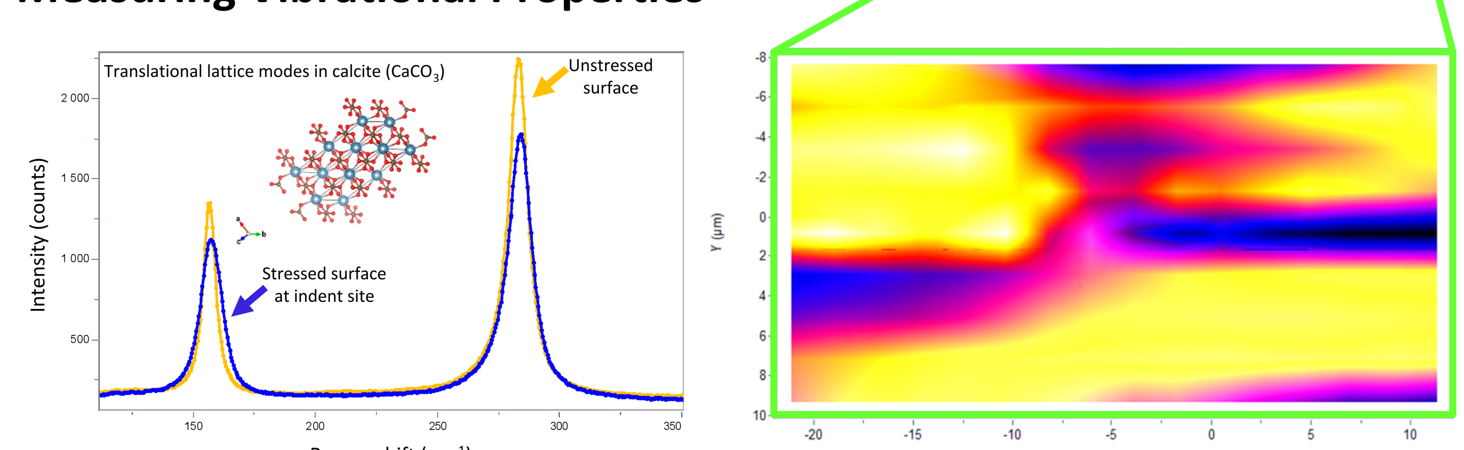
ReaxFF Equation for Total Energy (from [14]):

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb}$$

Measuring Nanomechanical Properties



Measuring Vibrational Properties



References

1. Lawn B. (1993). Fracture of Brittle Solids, 2nd edition, Eds.Davis E.A. and Ward FRS I.M., Cambridge University Press, ISBN 0521401763.
2. Bitzek E., Kermode J.R., and Gumbsch P. (2015). *International Journal of Fracture*, 191, 13-30.
3. Kermode J.R., Albaret T., Sherman D., Bernstein N., Gumbsch P., Payne M.C., Csanyi G., and De Vita A. (2008). *Nature Letters*, 455, 1224-1228.
4. Ilgen A.G., Mook B., Tigges A.B., Choens R.C., and Artyushkova K. (2018a) *Scientific Reports*, 8, 164656.
5. Ilgen A.G., Aman M., Espinoza D.N., Rodriguez M.A., Griego J.M., Dewers T.A., Feldman J.D., Stewart T.A., Choens R.C., and Wilson J. (2018b) *Int J Greenh Gas Control*, 78, 244-253.
6. Choens R.C., Wilson J., and Ilgen A.G. Submitted to *Earth and Planetary Science Letters.*
7. Griffith A.A. (1921). *Philosophical Transactions of the Royal Society of London A*, 221, 163-198.
8. Kermode J.R., Ben-Bashat L., Atrash F., Cilliers J.J., Sherman D., and De Vita A. (2013) *Nature Communications*, 4, 2441.
9. Atkinson B.K. and Meredith P.G. (1987). In: *Fracture Mechanics of Rock*, edited by Atkinson B.K., Elsevier Science.
10. Dunning J., Douglas B., Miller M., and McDonald S. (1994) *Pageoph*, 143, (1-3), 151-178.
11. Hu M. and Hueckel T. (2013) *Geotechnique*, 63, (4), 313-321.
12. Manzano H., Pellenq R.J.M., Ulm F.-J., Buehler M.J., Van Duin A.C.T. (2012) *Langmuir* 28 (9), 4187-4197.
13. Speziale S., Shieh S., and Duffy T.S. (2006) *J. Geophys. Res. Solid Earth* 111.B2.
14. Van Duin A. C.T., Dasgupta S., Lorant F., and Goddard W.A. (2001) *J. Phys. Chem. A* 105 (41), 9396-9409.
15. Sierra/SolidMechanics Team. Sierra/SolidMechanics 4.46 User's Guide. Technical Report SAND2017-9759, Sandia National Laboratories, Albuquerque, NM, 2017.

Exceptional service in the national interest

Sandia National Laboratories

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.SAND 2021-xxxx

Built on LDRD Laboratory Directed Research and Development
U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration