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Chemical controls on the propagation and healing of subcritical fractures

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ABSTRACT

Human activities involving subsurface reservoirs-resource extraction, carbon and nuclear waste storage-alter thermal, mechanical, and chemical steady-state conditions in these systems. Because these systems exist at lithostatic pressures, even minor chemical changes can cause chemically assisted deformation. Therefore, understanding how chemical effects control geomechanical properties is critical to optimizing engineering activities. The grand challenge in predicting the effect of chemical processes on mechanical properties lays in the fact that these phenomena take place at molecular scales, while they manifest all the way to reservoir scales. To address this fundamental challenge, we investigated chemical effects on deformation in model and real systems spanning molecular- to centimeter scales. We used theory, experiment, molecular dynamics simulation, and statistical analysis to (1) identify the effect of simple reactions, such as hydrolysis, on molecular structures in interfacial regions of stressed geomaterials; (2) quantify chemical effects on the bulk mechanical properties, fracture and displacement for granular rocks and single crystals; (3) develop initial understanding of universal scaling for individual displacement events in layered geomaterials; and (4) develop analytic approximations for the single-chain mechanical response utilizing asymptotically correct statistical thermodynamic theory. Taken together, these findings advance the challenging field of chemomechanics.

ACKNOWLEDGEMENTS

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ACRONYMS AND TERMS

Acronym/Term	Definition	
DFT	Density functional theory	
MD	Molecular dynamics	
MSF	Modular Force Stage	
RH	Relative humidity	

1. INTRODUCTION

Chemical reactions at individual crack tips can dramatically lower the failure envelope of crystalline phases making up sedimentary rocks, concretes, and ceramics. Subcritical fracture is a result of various chemically assisted processes, that are poorly understood. The importance of chemical effects on surface hardness and crack propagation has been recognized for several decades, and yet chemical mechanisms involved are still debated. To address these fundamental science unknowns we used theory, experiment, molecular dynamics simulations, and statistical analysis. The main goal of this research was to identify molecular mechanisms at solid-water interfaces that affect fracture, and to quantify how these molecular-scale processes affect the macroscopic fracture/deformation properties and observables at the laboratory scale.

The employed innovative combination of theoretical and experimental approaches (summarized in nine published and submitted papers, and in three manuscripts in preparation) advances our understanding of chemically assisted fracture. Here we focused on calcite – one of the most abundant carbonate minerals in the Earth's crust, and also included calcium oxide and layered phyllosilicate phases common in geomaterials. This new knowledge will lay the foundation for predicting and controlling cracks and fracture networks in natural and engineered systems. Applications include the development of chemical methods for sealing cracks (e.g., repairing caprock during CO₂ storage, repairing concrete), and for enhanced fracturing (enhanced geothermal systems).

To advance theoretical formulations describing chemical effects on fracture, we applied statistical thermodynamics and rigorous asymptotic approximations to an atomic model system for a crack (section 2). This resulted in useful analytic relations describing thermally-assisted crack growth that were verified with respect to existing subcritical crack growth experiments for glass (section 2.2). We also used this theoretical approach to model bond stretching in polymers (section 2.1) and molecular stretching in general (section 2.3) in order to demonstrate its broad applicability and effectiveness. To assess the role of water and hydrolysis reactions on the mechanical properties of calcium oxide and calcium carbonate we coupled molecular simulations with nanoindentation experiments (sections 3.1 and 3.2). These findings indicate that while calcium oxide is extremely susceptible to waterweakening, calcium carbonate is not. Using density functional theory (DFT) calculations, we show that water in fact can cause both weakening and strengthening of calcite at a crack tip, depending on whether water molecule is bridging nearby calcium atoms (section 3.4). This ambiguous effect of water on calcite fracture was also seen in our three-point bending tests (section 4.5) and in molecular dynamics (MD) simulations (section 3.3). Furthermore, we used compaction and triaxial deformation tests to assess the role of common anions in the bulk mechanical response arising from multitude of micron-scale cracks in individual grains (section 4.4). The results of these tests indicate that molecularscale processes at solid-water interfaces in fact are detectable at the core-scale of geomechanical tests. Finally, we combined nanoindentation experiments of layered phyllosilicate minerals in chemically reactive environments with detailed statistical analysis of displacement bursts and identified universal behaviors in the observed burst sequences, while chemical environment defined the exact burst characteristics and the onset of deformation (sections 4.1 and 4.2).

2. THEORY DEVELOPMENT

An asymptotic approach for statistical thermodynamics was successfully utilized to approximately solve a model system for a crack and obtain analytic relations describing subcritical crack growth. This approach is also shown to be applicable to polymer chains and molecular stretching in general.

2.1. Published paper: Freely Jointed Chain Models with Flexible Links

Citation:

Michael R. Buche, Meredith N. Silberstein, and Scott J. Grutzik (2022) Phys. Rev. E 106, 024502.

Abstract:

Analytical relations for the mechanical response of single polymer chains are valuable for modeling purposes, on both the molecular and the continuum scale. These relations can be obtained using statistical thermodynamics and an idealized single-chain model, such as the freely jointed chain model. To include bond stretching, the rigid links in the freely jointed chain model can be made extensible, but this almost always renders the model analytically intractable. Here, an asymptotically correct statistical thermodynamic theory is used to develop analytic approximations for the single-chain mechanical response of this model. The accuracy of these approximations is demonstrated using several link potential energy functions. This approach can be applied to other single-chain models, and to molecular stretching in general.

2.2. Submitted paper: A Statistical Mechanical Model for Crack Growth

Citation:

Michael R. Buche, Scott J. Grutzik (2023) arXiv:2212.00864.

Abstract:

Equations describing crack growth are useful for the modeling of experiments and increasing the theoretical understanding of fracture in general. Using an idealized model system for a crack and statistical thermodynamics, one can obtain the rate of thermally assisted crack growth in terms of the applied load, but the result is usually too complicated. An asymptotically correct theory is used here to produce analytic approximations of the crack growth rate in a rigorous fashion. These approximations are validated with respect to Monte Carlo calculations. This overall approach is applicable to future modeling efforts that might consider more complicated fracture mechanisms, such as inhomogeneity, a reactive environment, or viscoelastic relaxation from the bulk material.

A simple model system (see Figure 1) was constructed based upon models from the literature which were treated mechanically rather using statistical thermodynamics. The asymptotic approach [1-2] was applied and successfully obtained analytic relations for the crack growth velocity v as verified by Monte Carlo calculations. All numerical calculations were performed using statMechCrack [4]. In the thermodynamic limit of large system size and in the subcritical regime, the velocity simplified to

$$v = v_0 e^{-(\Delta u - f\Delta x)/kT} \sinh(Gb^2/2kT)$$

(1)

Here v_0 is a prefactor, Δu is the crack tip bond transition state energy, Δx is the distance to that transition state, k is the Boltzmann constant, T is the temperature, $f = \sqrt{GEb^3}$ is the effective force on the crack tip bond, G is the energy release rate, E is the modulus, and b is the bond length. Figure 1 shows Eq. (1) accurately predicting v measured in soda-lime silicate glass experiments [5].



Figure 1. The original model system for the crack (left) and the model prediction (solid) provided by Eq. (1) compared to subcritical crack growth experiments (circles) for soda-lime silicate (right).

2.3. Submitted paper: Modeling single-molecule stretching experiments using statistical thermodynamics

Citation:

Michael R. Buche, Jessica M. Rimsza (2023) arXiv: 2309.01009.

Abstract:

Single-molecule stretching experiments are used to characterize individual bonds or molecules. Equations describing these experiments are valuable and can be obtained using the statistical thermodynamics of idealized models. Since the thermodynamic ensembles imposed by the experiments change the outcome, the stretching device must be included in model, but including the device usually prevents analytic solutions. If the device is sufficiently stiff or compliant, the isometric or isotensional ensembles can provide approximations, but the device effects are then gone. A dual set of asymptotically correct theories are applied here to develop accurate approximations for the full model which includes both the molecule and the device. The asymptotic theories are demonstrated with a freely jointed chain and molecular dynamics calculations of polyethylene.

The molecular stretching experiment consists of an arbitrary molecule with the first end fixed, and the second end subject to a harmonic potential that models the stretching device, which is at a distance ξ from the first end. The partition function for the system would be

$$\boldsymbol{Q}(\boldsymbol{\xi}) = \iiint \boldsymbol{Q}_0(\boldsymbol{\xi}') \boldsymbol{e}^{-\frac{W(\boldsymbol{\xi}-\boldsymbol{\xi}')^2}{2kT}} d^3 \boldsymbol{\xi}'$$

(2)

W is the device stiffness, *k* is the Boltzmann constant, *T* is the temperature, ξ' is a dummy variable of integration, and Q_0 is the partition function of the molecule without the device in the isometric ensemble (both ends fixed at a distance ξ from each other). Using the asymptotic theory for steep potentials [1-3], the partition function is approximated for stiff devices as

$$Q(\xi) \propto Q_0(\xi) + \frac{kT}{2W} Q_0''(\xi)$$



Figure 2. Molecular dynamics calculations of polyethylene (solid) and asymptotic approximations (dotted) based upon the simpler reference system without the device (dashed). The expected force as a function of the potential distance for a stiff device (left), and the effective force as a function of the expected end-to-end length of the molecule for a compliant device (right).

The expected force f is calculated as a function of the potential distance ξ from Eq. (3) using

$$f(\xi) = -kT \ \frac{Q'(\xi)}{Q(\xi)}$$

The partition function and resultant mechanical response can be similarly approximated for compliant devices [6] using the asymptotic theory for weak potentials [7-8].

The approximations provided by the asymptotic theories become accurate in opposing limits: as the device stiffness becomes large compared to thermal energy and the instantaneous stiffness of the molecule, the asymptotic approximation for steep potentials i.e. Eq. (3) becomes accurate. As the device stiffness becomes small compared to thermal energy and the instantaneous stiffness of the molecule (and the device distance is large compared to the fluctuating length of the molecule), the asymptotic approximation for weak potentials becomes accurate. The order of the error can be estimated as $(\beta WL^2)^{-1}$ or βWL^2 for the two theories, respectively, where L is the molecule length. Both asymptotic theories were first demonstrated to become accurate in these limits using the freelyjointed chain model, where all calculations were performed using the Polymers Modeling Library [9]. Next, both asymptotic theories were demonstrated using molecular dynamics calculations of polyethylene using LAMMPS [10] and force fields from ReaxFF [11]. The results are shown in Figure 2. In the case of the stiff device ($W = 40 \text{ kJ/mol } \text{Å}^2$), the associated asymptotic approach is accurate until the polyethylene molecule reached high magnitudes of force under significant extension or compression. In the case of the compliant device ($W = 0.04 \text{ kJ/mol } \text{Å}^2$), associated asymptotic approach is accurate at higher forces, where the device would be significantly distant compared to the length of the molecule. In either case, the associated asymptotic approach is successful, but could be improved in the future by considering nonlinear effects of the device.

(4)

3. MOLECULAR SIMULATIONS

3.1. Published paper: Water Weakening of Calcium Oxide

Citation:

Rimsza J. and Ilgen A.G. (2022) Water Weakening of Calcium Oxide. J. Phys. Chem. C 2022, 126, 22, 9493–9501

Abstract:

Chemomechanical processes such as water weakening can control the permeability and deformation of rocks and manmade materials. Here, atomistic modeling and nanomechanical experiments were used to identify molecular origins of chemomechanical effects in calcium oxide (CaO) and its effect on observed elastic, plastic, and brittle deformation. Classical molecular dynamics simulations with the bond order-based reactive force-field ReaxFF were used to assess brittle fracture. In the presence of water, CaO fractured earlier and more often during quasi-static loading, with a calculated reduction in fracture toughness of ~80% associated with changes in the stress distribution around the crack tip. Experimentally, elastic and plastic deformation. Nanoindentation showed that following exposure to water, the contact hardness decreased by 1–2 orders of magnitude and decreased the modulus by 2–3 orders of magnitude due to surface hydroxylation. The strong chemomechanical effects on the mechanical processes in CaO suggests that minerals with similar structures may exhibit comparable effects, influencing the stability of cements and geomaterials [12].

3.2. Submitted paper: Anomalous Thermal Effects on Fracture in Anhydrous Amorphous Calcium Carbonate

Citation:

Rimsza J.M. and Ilgen A.G. Anomalous Thermal Effects on Fracture in Anhydrous Amorphous Calcium Carbonate <u>Submitted to J. Phys. Chem. C.</u>

Abstract:

Amorphous calcium carbonate (ACC) is a disordered phase of the common CaCO₃ polymorphs (calcite, aragonite, and vaterite) with critical roles in calcium carbonate cement properties. A fundamental understanding of how the structure of anhydrous ACC impacts the resulting mechanical and fracture properties was evaluated using classical molecular dynamics simulations with the reactive forcefield ReaxFF. Anhydrous ACC structures were generated through the compression of lowdensity mixtures of Ca²⁺ and CO₃²⁻ ions at varying rates, with slower compression rates resulting in increasing mechanical strength. Increases in the elastic constants were associated with decreasing Ca2+...Ca2+ coordination numbers and smaller Ca...Ca...C and Ca...Ca...O bond angles during slower compression rates. Fracture mechanisms of anhydrous ACC was evaluated under far-field loading conditions at varying temperatures. Surprisingly, at lower temperatures (0.1 K) cracks were 50% longer than at higher temperatures (150 K, 300 K) under the same externally applied load as seen in Figure 3. This temperature-dependency in crack growth arose from increased energy dissipation at higher temperatures, allowing for relaxation of the applied load without forming new surface area from crack growth. The energy dissipation mechanism was identified to include changes in the O. Ca. O bond angles between 40°-50° from conversion of Ca²⁺ ions from bidentate bound to a single CO₃²⁻ion to a bridging Ca²⁺ ion between two CO₃²⁻ion (Figure 3). The changing mechanism for fracture growth with increasing temperatures will influence the long-term stability of systems that contain calcium carbonate cements [13].



Figure 3. Change in crack depth during mechanical loading and fracture of anhydrous amorphous calcium carbonate (ACC) at 0.1 K, 150 K, and 300 K. Average and standard deviation of three unique starting configurations are included.

3.3. Submitted paper: Molecular Dynamics Simulations of Calcite Fracture in Water

Citation:

Wang Q., Rimsza J., Harvey J.A., Newell P., Gruenwald M., Ilgen A.G. Molecular Dynamics Simulations of Calcite Fracture in Water. <u>Submitted to J. Phys. Chem. C.</u>

Abstract:

Reactive molecular dynamics simulations were used to evaluate fracture of calcite (CaCO₃), including the impacts of initial notch geometry, the presence of water and surface hydroxyl groups. The fracture process in the absence and presence of water was assessed by comparing the loads where fracture began to propagate. The presence of a notch lowered the load where crack growth began the most, compared to the effects of water or surface hydroxyls. Importantly, the breaking of two adjacent Ca-O bonds is required crack initiation, since transiently broken bonds can re-form without crack growth. In the presence of water non-hydroxylated calcite surfaces exhibited water-strengthening; while after manual addition of either H⁺ and/or OH⁻ species on the calcite surface resulted in chemo-mechanical weakening by 9%. Full hydroxylation of the calcite surface was thermodynamically and kinetically limited, with only 0.17-0.01 OH/nm² of surface hydroxylation observed on the surface at the end of the simulations. Due to the limited reactivity of pure water with the calcite surface, we observed almost no effect of water on crack growth, suggesting that reactions between physiosorbed water and localized structural defects may be dominating the chemo-mechanical process in the experimental studies where water weakening has been reported [14].

3.4. Submitted paper: The Dual Nature of Surface Adsorbates on Fracture of Calcite

Citation:

Warner D.H., Grutzik S. and Ilgen A.G. The Dual Nature of Surface Adsorbates on Fracture of Calcite. <u>Submitted to Environmental Science and Technology Letters.</u>

Abstract:

We used ab-initio electronic structure calculations to determine the mechanisms by which surface adsorbates affect brittle fracture of calcite - a key failure mode of minerals. Unexpectedly, we found that adsorbates, such as water and ions can both enhance and inhibit the tendency to fracture, depending on the bonding configuration of the adsorbate to the calcite surface. Furthermore, the disassociation (hydrolysis) reaction of water at the calcite surface enhances its degrading effect on fracture. This mechanistic molecular picture establishes the feasibility for controlling the tendency of brittle minerals to fracture by manipulating the composition of secondary elements in environments and materials [15].

4. EXPERIMENTAL STUDIES

4.1. Published paper: Chemomechanical weakening of muscovite quantified with in situ liquid nanoindentation

Citation:

Mook W., Ilgen A.G., Jungjohann K., and DelRio F. (2022) Chemomechanical weakening of muscovite quantified with in situ liquid nanoindentation. Journal of Materials Science, 1-13

Abstract:

Chemomechanical weakening of layered phyllosilicate muscovite mica was studied as a function of chemical environment via in situ liquid-nanoindentation under four conditions (dry, deionized water, and two NaCl solutions of different pH). While traditional indentation analyses of layered materials with extreme mechanical anisotropy have been limited due to displacement bursts (pop-ins), here the bursts were used as proxies for delamination, fracture, and spalling events. Since displacement bursts during an indent represent a stochastic process, 120 indents were conducted for each condition to generate statistically significant amounts of data. In total, over 9000 bursts were assessed using a loaddisplacement threshold criterion, classifying this as a high-throughput nanoscale fracture technique. For each burst, initiation load, initiation displacement, plastic zone volume at initiation, and energy dissipation were analyzed. A power-law relationship between the burst load and burst energy was noted which separated the bursts into two continuous distributions: (1) bursts due only to the mechanics of the indent and (2) bursts due to both the mechanics of the indent and the environment. By using a cumulative probability distribution, it was found that the NaCl solutions decreased the minimum plastic zone volume necessary to initiate a displacement burst by an order of magnitude relative to the dry condition. Finally, the underlying mechanisms explaining the trends in initiation volume as a function of environment were discussed, with a focus on the chemomechanical degradation processes via chemical attack and cation exchange [16].

4.2. Manuscript prepared for submission: A simple micromechanical model quantifies chemomechanical weakening in nanoindented muscovite mica

Citation:

Sickle J., Mook W., DelRio F., Ilgen A.G., Wright W., and Dahmen K.A. A simple micromechanical model quantifies chemomechanical weakening in nanoindented muscovite mica. <u>Prepared for</u> submission.

Abstract:

Muscovite mica, one of the most common silicates on Earth, is frequently used in everyday applications from insulators in electronics to additives in makeup. One of this material's most striking properties is the anisotropy which emerges from its nearly perfect basal cleavage. Because of this anisotropy, the interplay between interfacial chemical processes on the mechanical response is poorly understood. Notably, the surface of muscovite can be susceptible to chemical attack by environmental hydroxyl ions. Previous work has shown that the characteristics of nanoindentation pop-in events are significantly influenced by the concentration of hydroxyl ions in its environment. However, a specific underlying physical model which could predict these changes was not determined.

We show that this observed change in the pop-in event statistics can be explicitly characterized with the same widely applicable physical model which describes the size and frequency of earthquakes. Additionally, we show that the statistics of events within this model are tuned by a weakening parameter the same way that altering the environmental hydroxyl concentration tunes the statistics of nanoindentation pop-in events in muscovite.

These are the first results to use this physical model to explicitly quantify chemomechanical weakening. The relative simplicity of the model used here allows these methods to be easily generalized to followup tests. Thus, these findings lay the groundwork for future studies to examine how chemomechanical effects can influence surface-mediated failures in a variety of contexts by using this physical model (Figure 4).



Figure 4. An overview of our findings; namely, that the weakening brought about on the surface of mica by OH ions is can be directly mapped to the weakening parameter in the same simple model that describes how earthquakes propagate.

4.3. Published paper: The Combined Effects of Mg²⁺ and Sr²⁺ incorporation during CaCO₃ precipitation and crystal growth

Citation:

Knight A.W., Harvey J.A., Shohel M., Lu P., Cummings D., and Ilgen A.G. (2023) The Combined Effects of Mg²⁺ and Sr²⁺ incorporation during CaCO₃ precipitation and crystal growth. <u>Geochimica et Cosmochimica Acta. 345, 16-33</u>

Abstract:

Calcite (CaCO₃) composition and properties are defined by the chemical environment in which CaCO₃ forms. However, a complete understanding of the relationship between aqueous chemistry during calcite precipitation and resulting chemical and physical CaCO₃ properties remains elusive; therefore,

we present an investigation into the coupled effects of divalent cations Sr^{2+} and Mg^{2+} on CaCO₃ precipitation and subsequent crystal growth. Through chemical analysis of the aqueous phases and microscopy of the resulting calcite phases in compliment with density functional theory calculations, we elucidate the relationship between crystal growth and the resulting composition (elemental and isotopic) of calcite. The results of this experimental and modeling work suggest that Mg2+ and Sr2+ have cation-specific impacts that inhibit calcite crystal growth, including: (1) Sr²⁺ incorporates more readily into calcite than Mg²⁺ ($D_{Sr} > D_{Mg}$), and increasing $[Sr^{2+}]_t$ or $[Mg^{2+}]_t$ increases D_{Sr} ; (2) the inclusion of Mg²⁺ into structure leads to a reduction in the calcite unit cell volume, whereas Sr²⁺ leads to an expansion; (3) the inclusion of both Mg^{2+} and Sr^{2+} results in a distribution of unit cell impacts based on the relative positions of the Sr²⁺ and Mg²⁺ in the lattice. These experiments were conducted at saturation indices of $CaCO_3$ of ~4.1, favoring rapid precipitation. This rapid precipitation resulted in observed Sr isotope fractionation confirming Sr isotopic fractionation is dependent upon the precipitation rate. We further note that the precipitation and growth of calcite favors the incorporation of the lighter ⁸⁶Sr isotope over the heavier ⁸⁷Sr isotope, regardless of the initial solution conditions, and the degree of fractionation increases with D_{Sr}. In sum, these results demonstrate the impact of solution environment to influence the incorporation behavior and crystal growth behavior of calcite. These factors are important to understand in order to effectively use geochemical signatures resulting from calcite precipitation or dissolution to gain specific information [17].

4.4. Manuscript in preparation: Surface chemistry effects on the consolidation of oxide-based geomaterials

Citation:

Choens, R.C., Wilson, J., Ilgen, A.G. Surface chemistry effects on the consolidation of oxide-based geomaterials. <u>Prepared for submission</u>.

Abstract:

Here, we extend our surface complexation hypothesis to new oxide based geomaterials. Previously, we demonstrated that subcritical crack growth in calcite can be controlled by the affinity of anions in solution to form surface complexes with Ca^{2+} in the crack surface, essentially drying out the crack tip by outcompeting water for access. Here, we test this hypothesis for homogenous grain packs of oligoclase and multi-phase samples of Torrey Buff sandstone. Samples of oligoclase were deformed under hydrostatic consolidation, demonstrating that the addition of ions that could form surface complexes with Ca^{2+} lead to strengthening compared to de-ionized water saturated samples, showing that in addition to calcite [18] this mechanism is also applicable to Ca-containing silicate oligoclase. 1D consolidation experiments on Torrey Buff sandstone demonstrated a clear water weakening effect, as all fluid saturated experiments were weaker than dry experiments (Figure 5). Differences between brines and de-ionized water are less clear, as microfracture measurements show the chemistries that strengthened one phase weakened another, leading to mixed results. Experiments highlight the complexity and need for understanding of geochemical processes when designing treatments to control subsurface behavior.



Figure 5. a) Calculated surface energy based on microstructural measurement for Torrey Buff sandstone dependent on fluid type. b) Measured strain energy and measured strain energy to specific surface energy ratio dependent on fluid type.

4.5. Manuscript in preparation: Fracture Propagation in Calcite Under Defined Humidity Conditions

Citation:

Wilson, J.E. and Ilgen, A.G. Fracture Propagation in Calcite Under Defined Humidity Conditions. In preparation.

Abstract:

Fracture experiments were performed on notched calcite monocrystals to investigate the effect of humidity on fracture propagation. Previous investigations quantify effects on subcritical fracture propagation in calcite using double torsion point loading in the presence of varying fluid chemistries (Bergsaker et al., 2016; Rostom et al., 2012). Our novel approach uses a 3-point bend loading configuration (Figure 6a) to investigate mode I fracture propagation under varying humidity levels. A Linkam Modular Force Stage (MFS) is used to apply load with Link software controlling jaw movement and allowing precise measurement of compressive loading force. Linkam RH95 controls and monitors humidity within the MFS and LabSpec6 imaging software was used with Xplora Raman Microscope to view fracture tip propagation optically at 100X total magnification (Figure 6b). To induce fracturing, a notch was machined into each calcite plate; this notch was aligned parallel to the 3rd point in the 3-point loading experiment (Figure 6a).

Each successful experiment includes (1) propagation—loading of the sample until a pre-existing fracture propagates, (2) relaxation—pause in loading to allow fracture and load to stabilize, (3) healing—unloading of the sample for select experiments, and (4) completion—loading of sample until

dynamic fracture breaks sample in two. Compressive loading force is measured during each stage (Figure 6c,d) and change in fracture length is measured during the relaxation stage (Figure 6e). Initial data analysis of experiments at 10%, 40%, and 80% RH shows mixed results. Loading force required for fracture propagation does not systematically increase or decrease with humidity. Likewise, additional loading force and time required to reach relaxation stage (100 microns of fracture growth) do not show consistent correlation with humidity levels. Additional data processing from experiments run in triplicate, as well as calculation of fracture tip velocity and energy release rate may reveal correlations between fracture behavior and humidity conditions.



Figure 6. (a) MFS setup on Raman microscope, allowing imaging of fracture propagation at 100X magnification using LabSpec6 software. Calcite monocrystal is in place between 3-point bend grips that are lined with silicone rubber to prevent crushing of calcite at grip points. Controlled movement of the grips induces a load on the calcite plate, causing the pre-existing fracture to propagate and then relax (propagation slows and load decreases over time). (b) LabSpec6 image of propagating fracture tip (circled). Length of microfracture over time is measured from screenshots during relaxation period (2 hours). Image width = 1 mm. (c) Loading path during a full experiment. (d) Variation in loading force from onset of fracture propagation through the 2-hour relaxation stage. (e) Change in fracture length during relaxation stage.

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