Fluid chemistry and fracture growth: what’s the connection?

Project Officer: Bill Vandermeer
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Relevance/Impact of Research

• **Objective/Purpose**
  – Apply new approaches to study subcritical crack growth (SCG)
    • Hydrothermal Atomic Force Microscope (HAFM)
    • Vertical Scanning Interferometer (VSI)

• **Technical Target**
  – Understand interplay of: stress, chemistry and T on crack growth
  – Is Dove’s (1995) Model appropriate?

• **Supports GTO objectives**
  – Enhance understanding of mechanical, thermal, chemical evolution of natural and induced fractures

• **Relevancy/impact**
  – EGS reservoir stimulation and long term heat extraction
  – Understand depth-dependent brittle/ductile transition
  – Applies to induced seismicity, shear slip of existing fractures and earthquake cycles
Scientific/Technical Approach
Chemistry & mechanics: connection at the nanoscale

- Impact of chemistry is greater at low stresses
- Low, long-term stresses are characteristic of many geologic phenomena and engineered systems

(Michalske and Bunker, 1987)

(Atkinson, 1984)
Breakage of Si-O bridging bonds controls fracturing and dissolution

Acid to Neutral pH

\[ >\text{Si-O-Si} < + \text{H}_2\text{O} = \uparrow = 2>\text{SiOH} \]

Basic pH

\[ >\text{Si-O-Si} < + \text{OH}^- = \uparrow = >\text{SiOH} + >\text{SiO}^- \]

- Dove’s (1995) hypothesis: Chemical reactions that control dissolution kinetics of quartz also impact solvent-surface interactions at the crack tip and thus control subcritical fracture kinetics
- Clear evidence exists for influence of chemistry on subcritical crack growth
- Existing data is limited in T and composition space and inadequate to develop models that link chemistry and fracture mechanics
Dove’s (1995) rate law

- Crack velocity varies with stress intensity factor ($K\text{\textsubscript{I}}$), temperature ($T$), pH and fluid composition (through its impact on surface chemistry)

\[
r_{\text{Si-O}} = A_{H\text{\textsubscript{2}}O} \exp\left(-\frac{\Delta H^{\text{sp}}_{H\text{\textsubscript{2}}O}}{RT}\right) \exp(b^{*}_{H\text{\textsubscript{2}}O} K_{I}(\Theta^{H\text{\textsubscript{2}}O}_{\text{Si-O}})) + A_{OH^{-}} \exp\left(-\frac{\Delta H^{\text{sp}}_{OH^{-}}}{RT}\right) \exp(b^{*}_{OH^{-}} K_{I}(\Theta^{OH^{-}}_{\text{Si-O}}))
\]

where:

- $r_{\text{Si-O}}$ = macroscopic fracture rate (ms\textsuperscript{-1})
- $A_{i}$ = pre-exponential term for the $i$\textsuperscript{th} mechanism (ms\textsuperscript{-1})
- $\Delta H^{\text{sp}}_{i}$ = experimentally determined activation enthalpy for the $i$\textsuperscript{th} mechanism (kJ mol\textsuperscript{-1})
- R = Universal gas constant, 8.3144 (J mol\textsuperscript{-1} K\textsuperscript{-1})
- $T$ = temperature (K)
- $b^{*}_{i} = b_{i}/RT$ and $b_{i}$ = geometry term for the crack tip and $i$\textsuperscript{th} mechanism (J mol\textsuperscript{-1})
- $K_{I}$ = stress intensity factor (N m\textsuperscript{3/2})
- $\Theta^{H\text{\textsubscript{2}}O}_{\text{Si-O}}$ = fraction of Si-O bonds reacting with molecular water
- $\Theta^{OH^{-}}_{\text{Si-O}}$ = fraction of Si-O bonds reacting with hydroxyl ions

As $T$ increases, impact of chemistry increases.
More data needed to develop generalized SCG models

- Only quartz has been studied in enough detail to suggest a constitutive relationship
- No fracture growth data available above 80ºC
- Fluid chemistry in fracture tests often unknown
  - Measured pH effects are limited to strong acid or base treatments
  - Low concentrations of salts in near-neutral pH solutions may cause large increases in fracture rates in quartz (based on dissolution kinetics effects) - but little data available

Hydrothermal atomic force microscopy: A new technique for obtaining data for developing constitutive relationships
Hydrothermal AFM

- 150° C & 10 atm in Ti flow cell
- AFM/LFM TopView© Optical Head
  - Allows frictional force measurement
  - Allows optical microscope imaging
- Molded Kalrez membrane
  - Minimize hysteresis
  - Better thermal stability
- Large custom piezo
  - 130µ scan range
- Pico-motor X-Y translator
  - Move piezo ± 1mm in <0.1µ steps
- Ti mini bending jig
  - Apply stress to sample while imaging
  - Study connection between chemistry and mechanics
- Tall Ti flow cell for mini jig
- Etched foil heater
  - More rapid heating/cooling and better T control
- OH base plate with cooling capability
Vickers indenter creates initial cracks

- Float glass is being used for initial testing
- Small cracks (~ 5 - 20 μ) initiated in air using a Vickers indenter (20 N for 15 sec)
Bending jigs designed and tested

5X bending jig

Bending stress applied  Neutral position

Correct scale bending jig

1 cm
Stress intensity factor ($K_I$) is calculated from curvature of sample in bending jig

- Radius of curvature (R) allows calculation of $K_I$

$$\sigma = \frac{E}{R}(h/2)$$

$$K_I = \sigma \left(\pi c\right)^{1/2} f_1 f_2$$

$\sigma = \text{stress}$
$E = \text{Young's modulus} = 70.3 \times 10^9 \text{ Pa for our glass}$
$h = \text{thickness of sample}$
$c = \text{crack length at the surface}$
$f_1 = \text{elliptical shape factor (0.64 - 1)} = 0.64 \text{ for our case}$
$f_2 = \text{effect of front free face (1 - 1.12)} = 1.0 \text{ for our case}$

- Curvature of glass in jig measured with white light vertical scanning interferometry (VSI)
- Symmetrical bending validates design of bending jig
- Attach heating device to measure curvature at elevated temperature
Symmetrical bending validates performance of mini-bending jig: VSI results

X-range 1.2 mm
Y-range 915 µm

R = 9045 mm

R = 441 mm
FE Modeling of mini-bending jig

- Confirmed that observed behavior of minijig is “predicted”
  - Vertical strain field and displacement are linear near crack
  - Bowing observed in jig is “predicted” using 3D FE model
- Comsol Multiphysics package
Appropriate range of the stress intensity factor ($K_I$) is produced by the bending jig

- $K_I = 2.5 \times 10^{-2}$ to $7.2 \times 10^{-1}$ MPa-m$^{1/2}$
  - Radius of curvature from 8018 to 285 mm in glass
  - Solution for a “half penny” crack perpendicular to a flat surface
  - 0.103 cm thick glass plate
  - ~20 µm crack length
  - Young’s modulus
    - 70.3 GPa for float glass
    - 73 GPa for fused silica
    - 76.5-97.2 GPa for quartz
    - 80 GPa for calcite

Experimentally accessible range with HAFM
Accomplishments, Results and Progress

S#13  ROC = 0.91 m  $K_i = 3.24 \times 10^5 \text{ Pa} \cdot \text{m}^{1/2}$

Conditions investigated:
$T = 25 ^\circ \text{C}$; $P = 2 \text{ bar}$; pH = 9.0 and $I = 0.001 \text{ M}$

Crack propagated at velocity = 9.1 µm/h
Accomplishments, Results and Progress

- Prepared & characterized glass samples at LBL
  - Cut and milled float glass samples to size at LBL for bending jig
  - Initiated cracks using LLNL Vickers Indenter – none available at LBL
    - LLNL chemist frequently unavailable, progress hindered
  - Pre-test VSI images collected on all samples

- Trained postdocs on use of VSI, HAFM and bending jig
  - Initial postdoc subsequently hired by University of Toulouse, France
    - Left during 4th quarter of FY14, underran budget, progress hindered

- Continued glass SCG experiments
  - Used LBL Zygo interferometer to measure radius of curvature needed for calculation of stress intensity factor
  - Ran SCG experiments in HAFM using mini-bending jig at different stress intensity factor levels
  - Pace picking up as new postdoc becomes proficient
  - Now completing glass runs at elevated T and then will begin novaculite SCG runs

Completed 5 series of experiments over a range in stress intensity factors, including movies of crack growth

<table>
<thead>
<tr>
<th>Original Planned Milestone/ Technical Accomplishment</th>
<th>Actual Milestone/Technical Accomplishment</th>
<th>Date Completed</th>
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<tbody>
<tr>
<td>Prepare samples, initiate cracks using Vickers Indenter, characterize glass using VSI, conduct SCG experiments as ( f(K_i, \text{chemistry}, T) )</td>
<td>System assembled and tested, glass samples prepared, cracks initiated, conducted SCG experiments</td>
<td>Fall 2014</td>
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<tr>
<td>Complete glass SCG experiments, start quartz experiments, verify Dove model</td>
<td>Glass SCG experiments continue, novaculite has been obtained to test Dove model</td>
<td>In progress</td>
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Future Directions

- Present research direction
  - Complete SCG experiments as proposed with glass as $f(K_i, \text{chemistry}, T)$
  - Continue SCG experiments as proposed with novaculite (quartz) as $f(K_i, \text{chemistry}, T)$
  - Verify that Dove (1995) Model is appropriate using quartz
  - HAFM-based crack velocity can be measured, but with poor efficiency due to inherent AFM “shutter speed” and FOV limitations

- Future direction
  - LBL formally part of recently funded French Soultz-sous-Forets geothermal research to develop VSI/PSI-based flow reaction cell that could dramatically improve SCG velocity measurements
  - Piggy-back our SCG geothermal research by designing bending jig to fit VSI/PSI-based flow reaction cell

### Milestone or Go/No-Go FY15 remaining & FY16 (no-cost extension?)

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<th>Status and expected completion date</th>
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<tr>
<td>Currently procuring novaculite (quartz), expect HAFM-based SCG experiments complete 10/15</td>
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<tr>
<td>French project recently funded, initiating collaboration now</td>
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- Prepare samples, initiate cracks using Vickers Indenter, characterize novaculite using VSI, conduct SCG experiments as $f(K_i, \text{chemistry}, T)$ – verify Dove Model
- Develop VSI/PSI-based SCG approach with French Soultz-sous-Forets collaborator
We have successfully developed an HAFM-based approach to SCG velocity measurement:

- Crack velocity measured as $f(K_i, \text{chemistry, T})$
- Using soda lime glass as test vehicle, we showed that results are comparable to previous SCG results based on optical methods acquired (typically) at larger scale
- AFM-based approach better suited to mechanistic studies via post-mortem examination, rather than crack velocity measurement:
  • Brittle-ductile transition
  • Crack arrest and re-initiation (lag)
  • Crack displacement
  • Role of cavity formation (if any) in crack propagation

We plan to develop a VSI/PSI-based approach to SCG velocity measurement:

- Piggyback these SCG geothermal studies with French research group working on Soultz-sous-Forêts geothermal site