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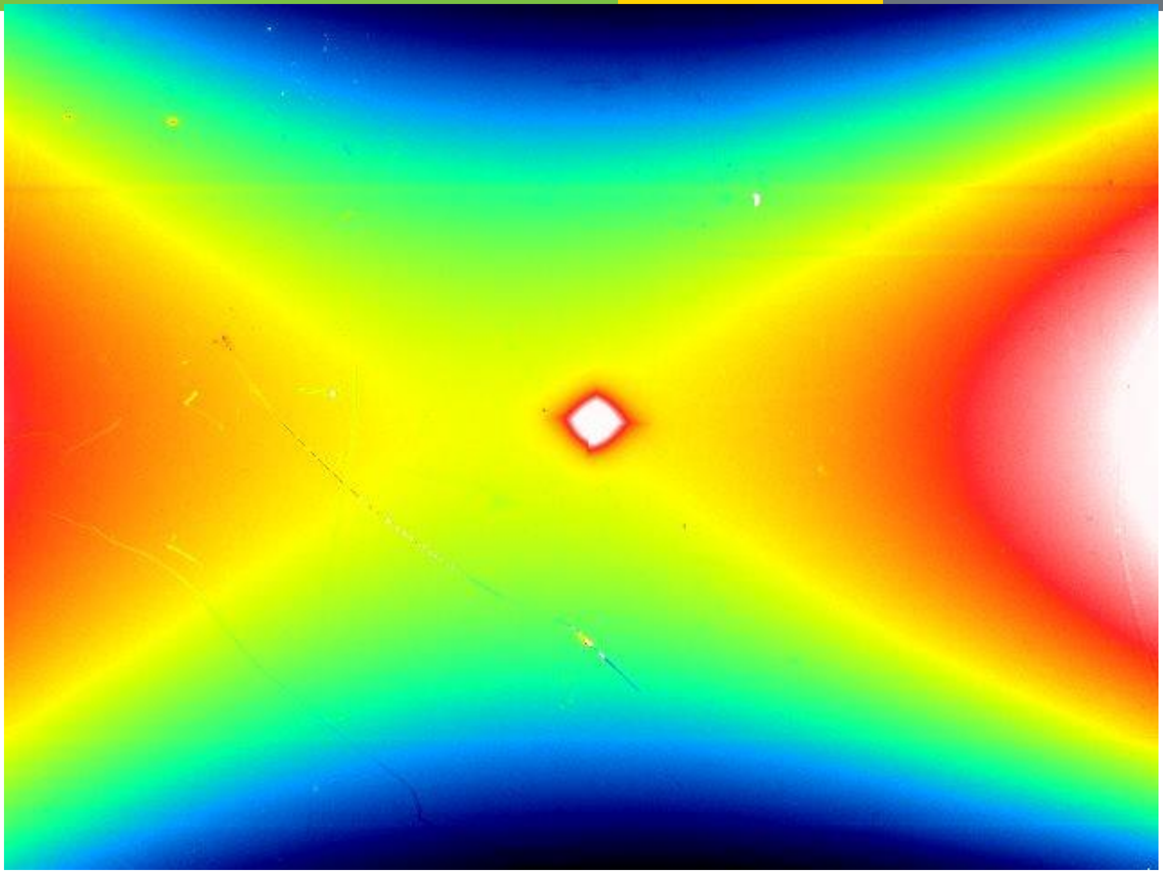

Fluid chemistry and fracture growth: what's the connection?

Project Officer: Bill Vandermeer

Total Project Funding: $185k/y

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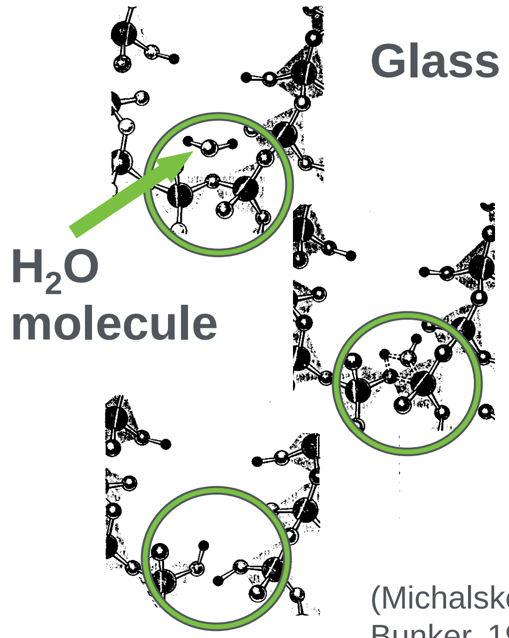
Relevance/Impact of Research

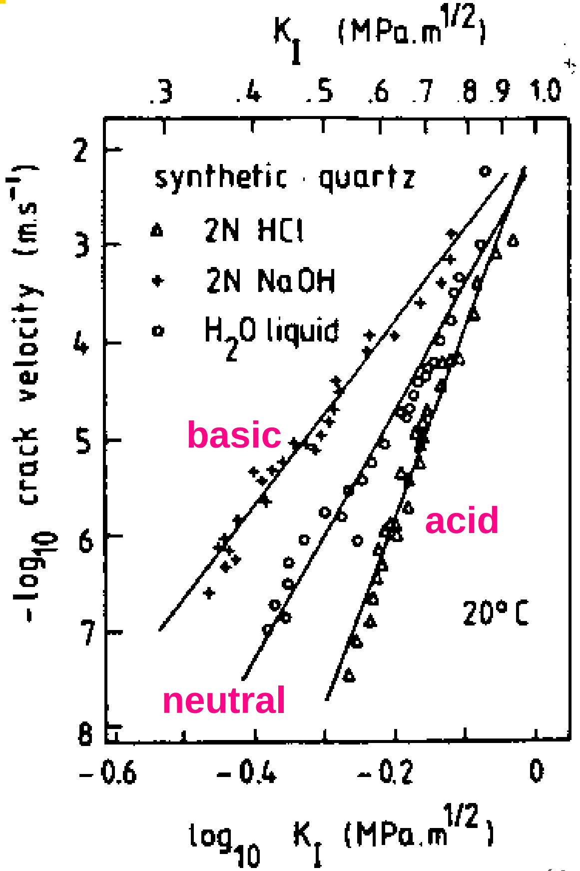
- Objective/Purpose
  - Apply new approaches to study subcritical crack growth (SCG)
    - Hydrothermal Atomic Force Microscope (HAFM)
    - Vertical Scanning Interferometer (VSI)
- Technical Target
  - Understand interplay of: stress, chemistry and T on crack growth
  - Is Dove's (1995) Model appropriate?
- 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



(Michalske and Bunker, 1987)



(Atkinson, 1984)

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

Breakage of Si-O bridging bonds controls fracturing and dissolution

Acid to Neutral pH

$$>Si\text{-}O\text{-}Si< + H_2O = \ddagger = 2>SiOH$$

Basic pH

$$>Si\text{-}O\text{-}Si< + OH^- = \ddagger = >SiOH + >SiO^-$$

- 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_I,), temperature (T), pH and fluid composition (through its impact on surface chemistry)

$$r_{Si-O} = A_{H_2O} \exp\left(\frac{-\Delta H^{xp}_{H_2O}}{RT}\right) \exp\left(b^*_{H_2O} K_I\right)\left(\Theta^{H_2O}_{Si-O}\right) + A_{OH^-} \exp\left(\frac{-\Delta H^{xp}_{OH^-}}{RT}\right) \exp\left(b^*_{OH^-} K_I\right)\left(\Theta^{OH^-}_{Si-O}\right)$$

where: r_{Si-O} = macroscopic fracture rate (ms^{-1})

A_i = pre-exponential term for the i^{th} mechanism (ms^{-1})

ΔH^{xp}_i = experimentally determined activation enthalpy for the i^{th} mechanism (mol^{-1})

R = Universal gas constant, 8.3144 (J mol^{-1} K^{-1})

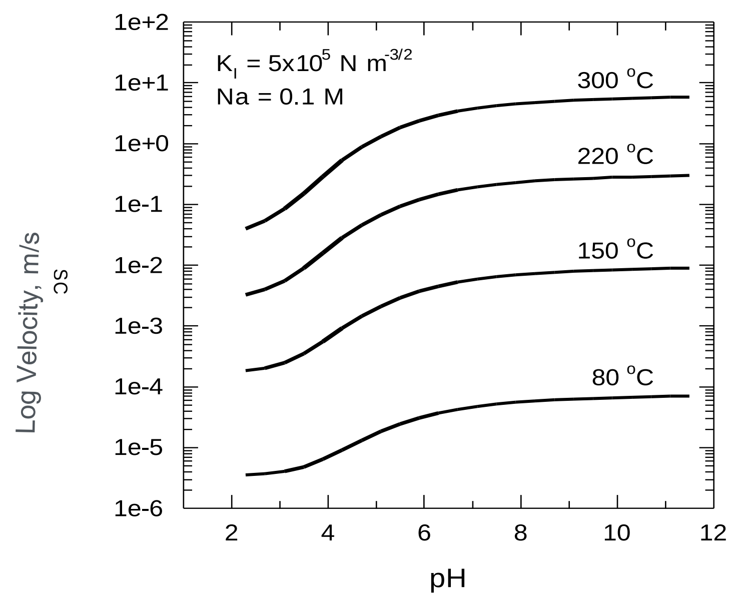
T = temperature (K)

b^*_i = b_i/RT and b_i = geometry term for the crack tip and i^{th} mechanism (J mo

K_I = stress intensity factor (N m$^{-3/2}$)

$\Theta^{H_2O}_{Si-O}$ = fraction of Si-O bonds reacting with molecular water

$\Theta^{OH^-}_{Si-O}$ = fraction of Si-O bonds reacting with hydroxyl ions



(Bonner and Viani, 2001)

As T increases, impact of chemistry increases

More data needed to develop generalized SCG models

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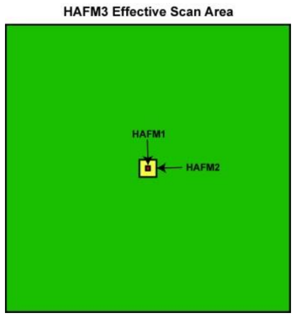
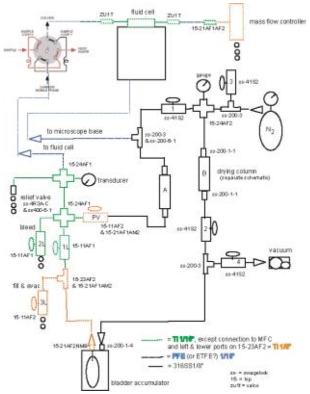
- Only quartz has been studied in enough detail to suggest a constitutive relationship
- No fracture growth data available above 80ºC
- Fluid chemistry in fracture tests often unknown
  - Measured pH effects are limited to strong acid or base treatments
  - Low concentrations of salts in near-neutral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

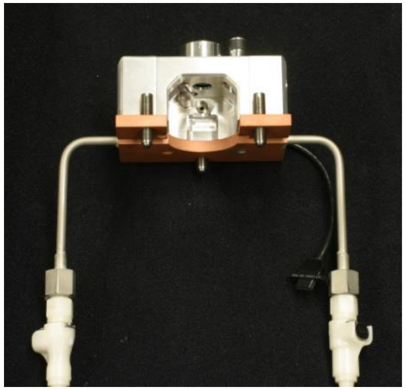
Hydrothermal atomic force microscopy: A new technique for obtaining data for developing constitutive relationships

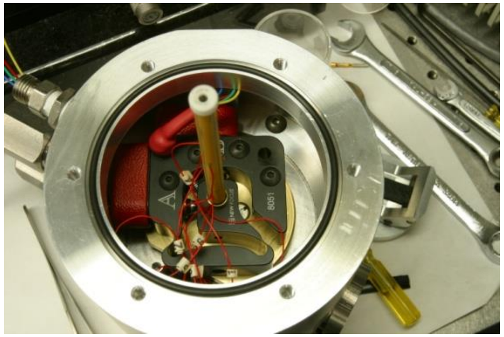
Hydrothermal AFM

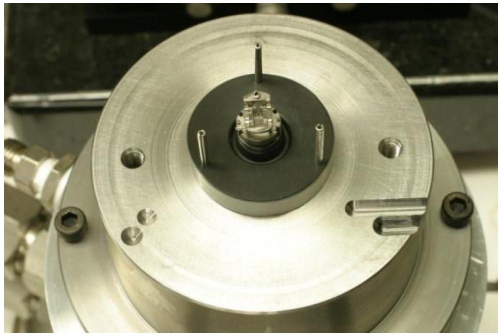
- 150° C & 10 atm in Ti flow cell
- AFM/LFM TopView© Optical Head
  - Allows frictional force measurement
  - Allows optical microscope imaging
- Molded Kalrez membrane
  - Minimize hysteresis
  - Better thermal stability
- Large custom piezo
  - 130µ scan range
- Pico-motor X-Y translator
  - Move piezo ± 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

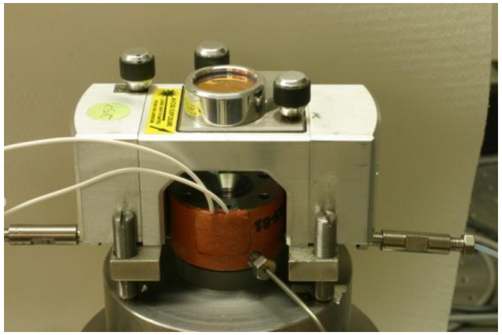


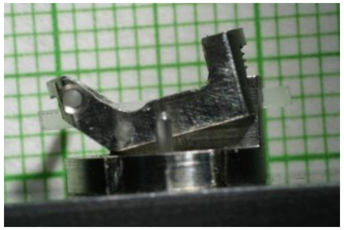


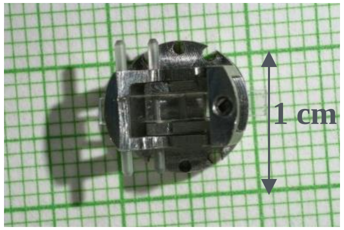




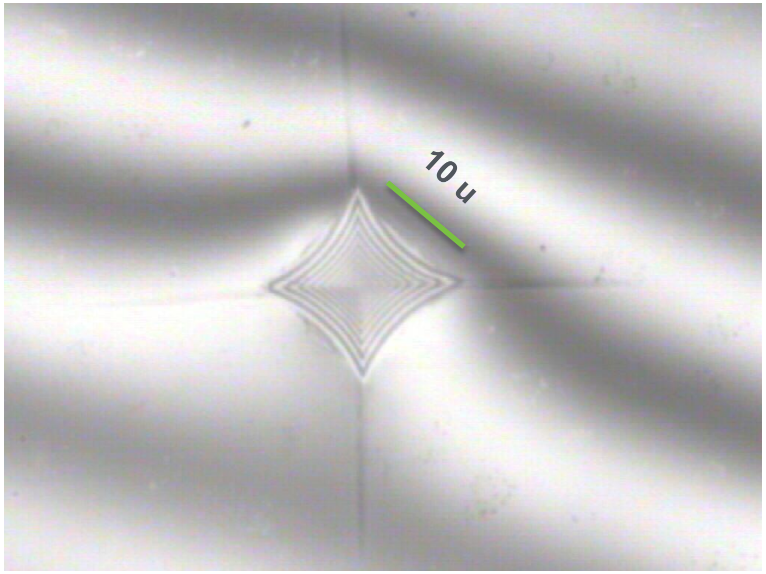




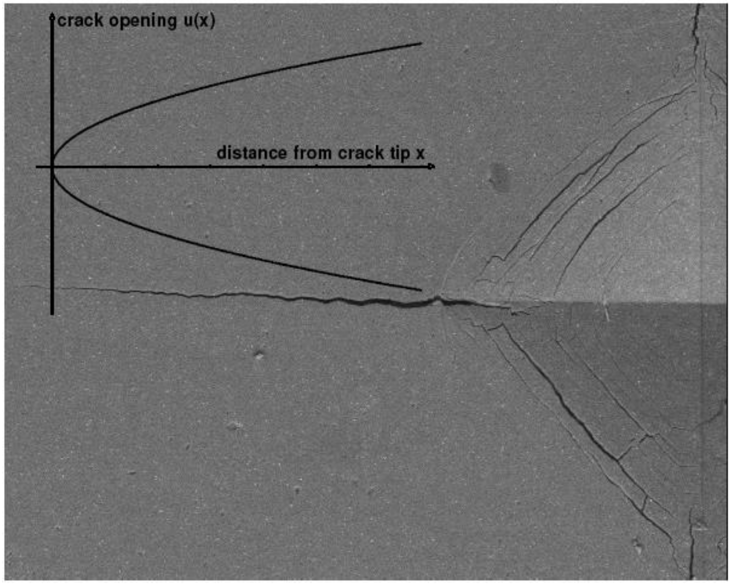




Vickers indenter creates initial cracks



Float glass (Knauss)

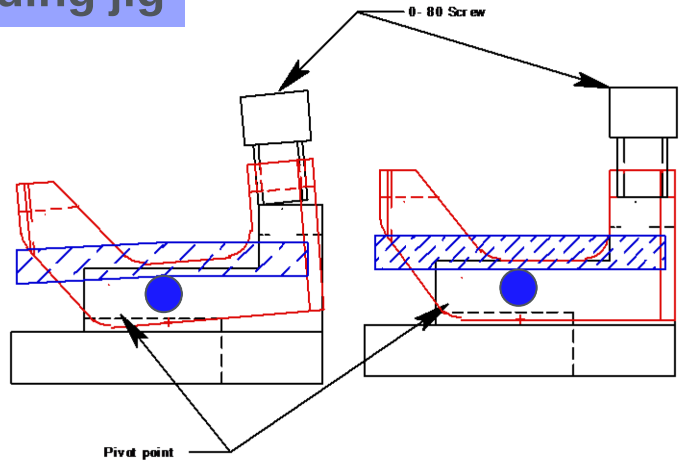


Ceramic (Marx et al., 2004)

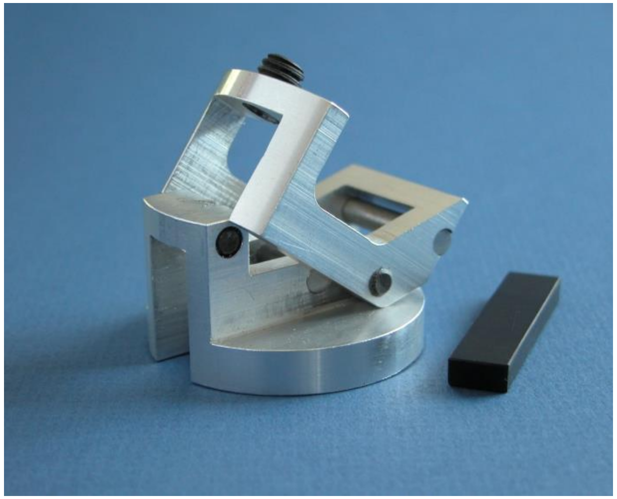
- Float glass is being used for initial testing
- Small cracks (~ 5 - 20 μ) initiated in air using a Vickers indenter (20 N for 15 sec)

Bending jigs designed and tested

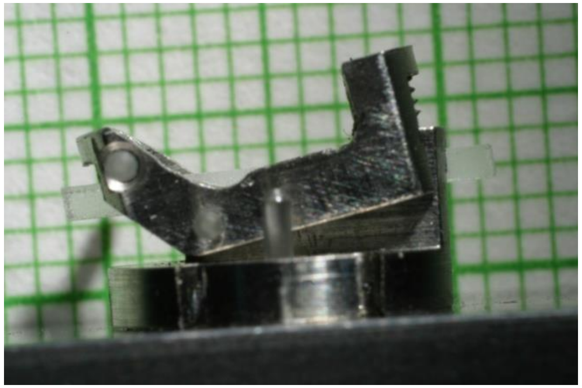
5X bending jig

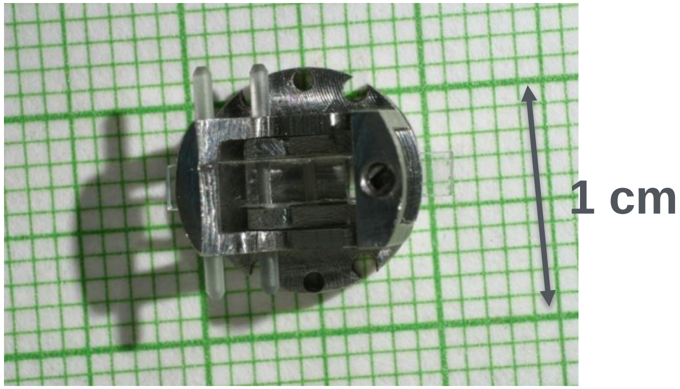


Bending stress applied   Neutral position



Correct scale bending jig





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

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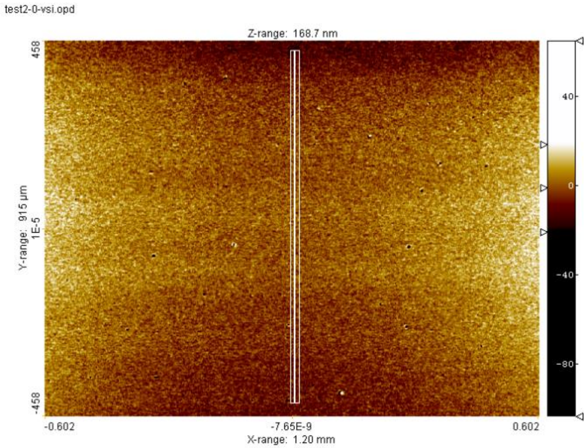
- Radius of curvature (R) allows calculation of K_I

  $\sigma = (E/R)(h/2)$

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

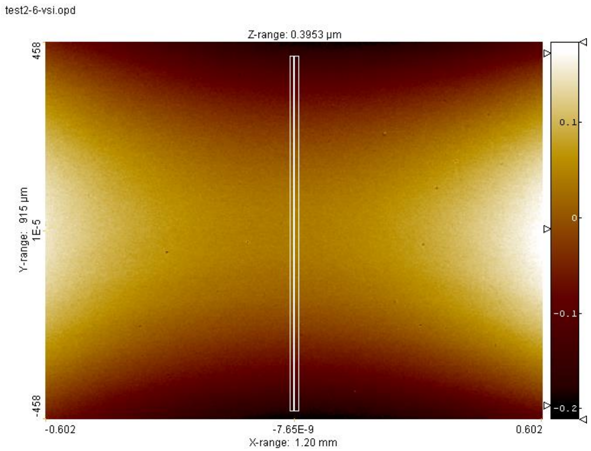
  - σ = stress
  - E = Young's modulus = 70.3×10^9 Pa for our glass
  - h = thickness of sample
  - c = crack length at the surface
  - f_1 = elliptical shape factor (0.64 - 1) = 0.64 for our case
  - f_2 = effect of front free face (1 - 1.12) = 1.0 for our case
- Curvature of glass in jig measured with white light vertical scanning interferometry (VSI)
- Symmetrical bending validates design of bending jig
- Attach heating device to measure curvature at elevated temperature

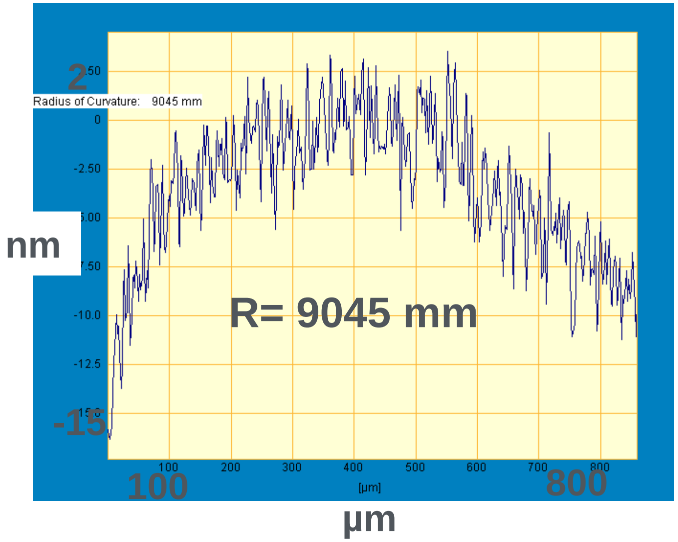
Symmetrical bending validates performance of mini-bending jig: VSI results

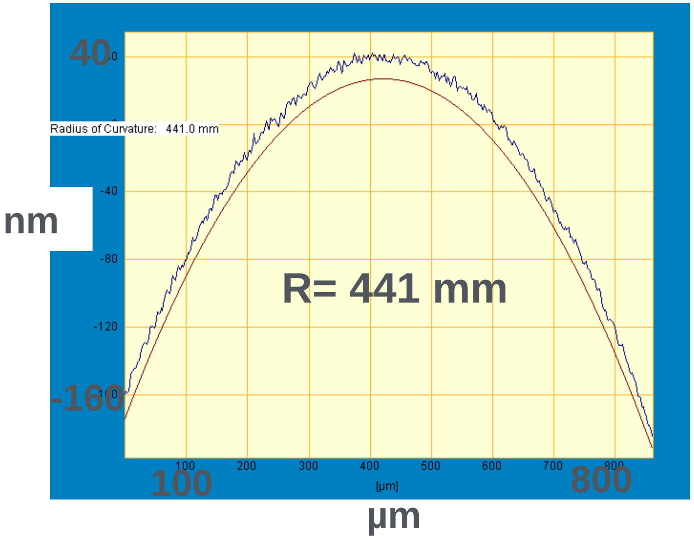


X-range 1.2 mm

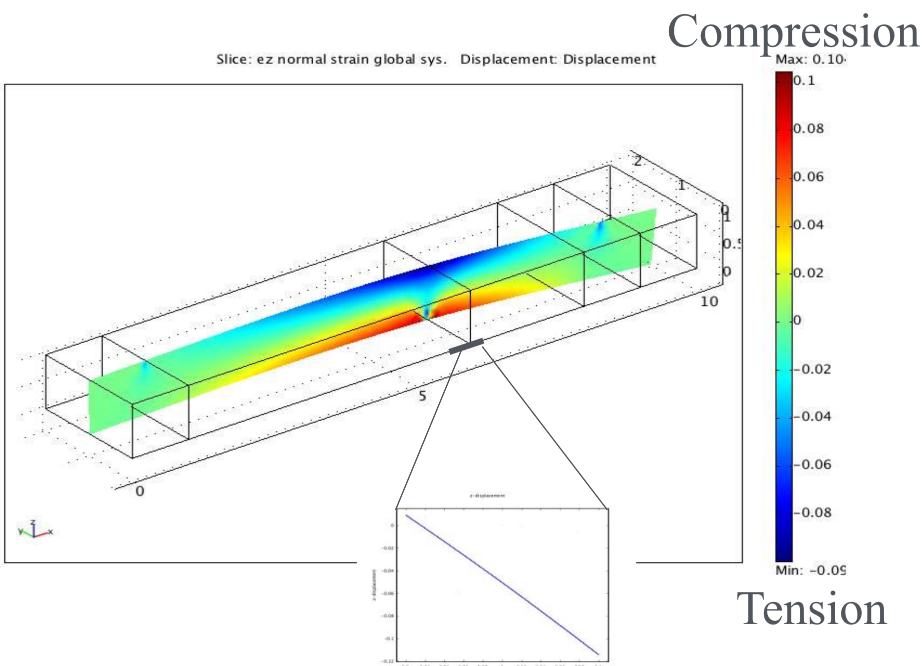
Y-range 915 µm

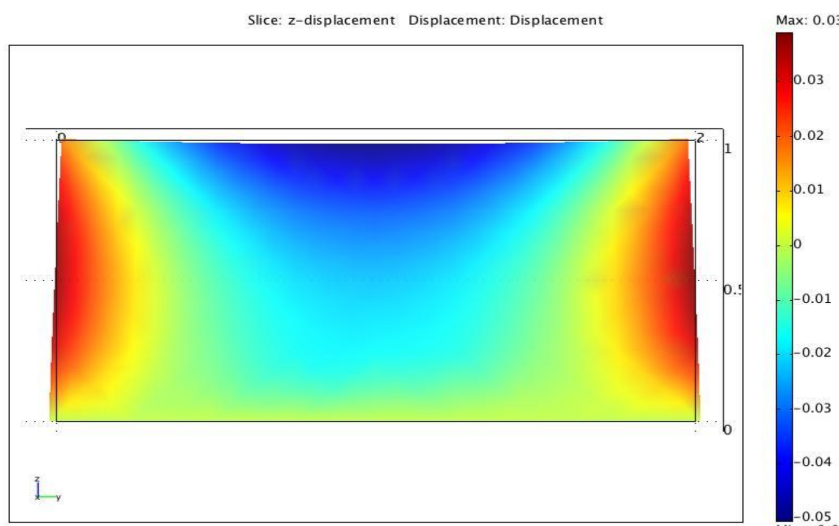






- Confirmed that observed behavior of minijig is “predicted”
  - Vertical strain field and displacement are linear near crack
  - Bowing observed in jig is “predicted” using 3D FE model
    - Comsol Multiphysics package





Appropriate range of the stress intensity factor (K_I) is produced by the bending jig

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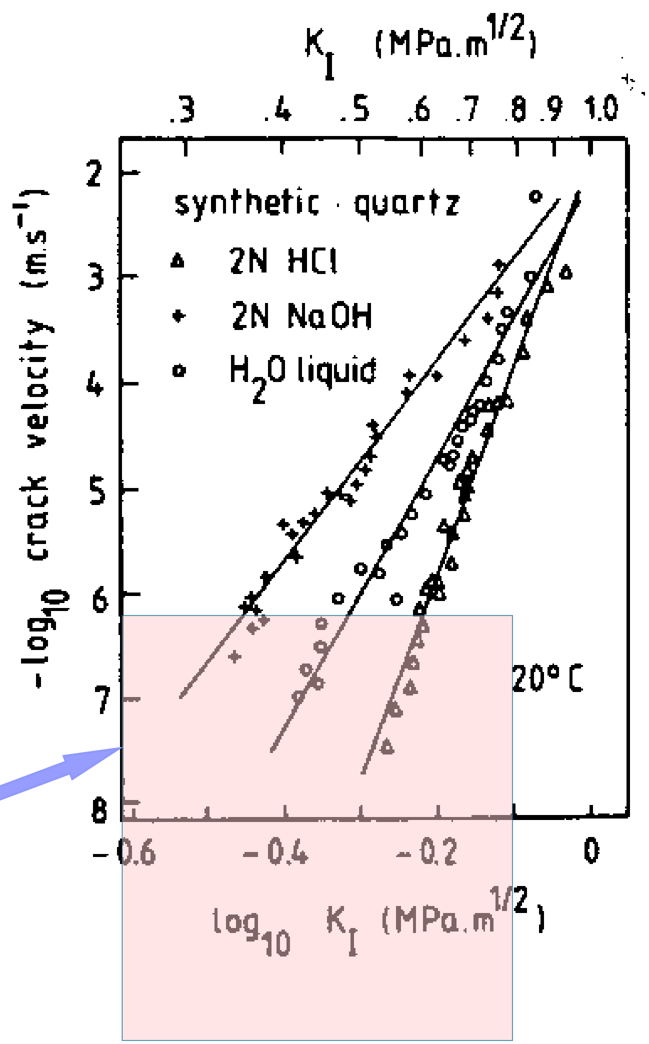
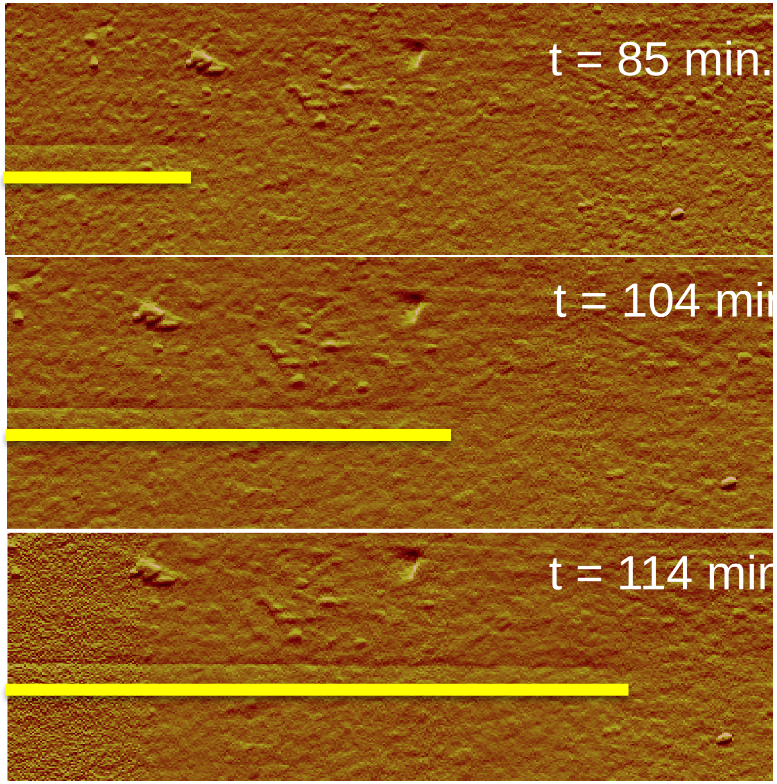
- K_I = 2.5×10^{-2} to 7.2×10^{-1} MPa-$m^{1/2}$
  - Radius of curvature from 8018 to 285 mm in glass
  - Solution for a "half penny" crack perpendicular to a flat surface
  - 0.103 cm thick glass plate
  - ~ 20 µm crack length
  - Young's modulus
    - 70.3 GPa for float glass
    - 73 GPa for fused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

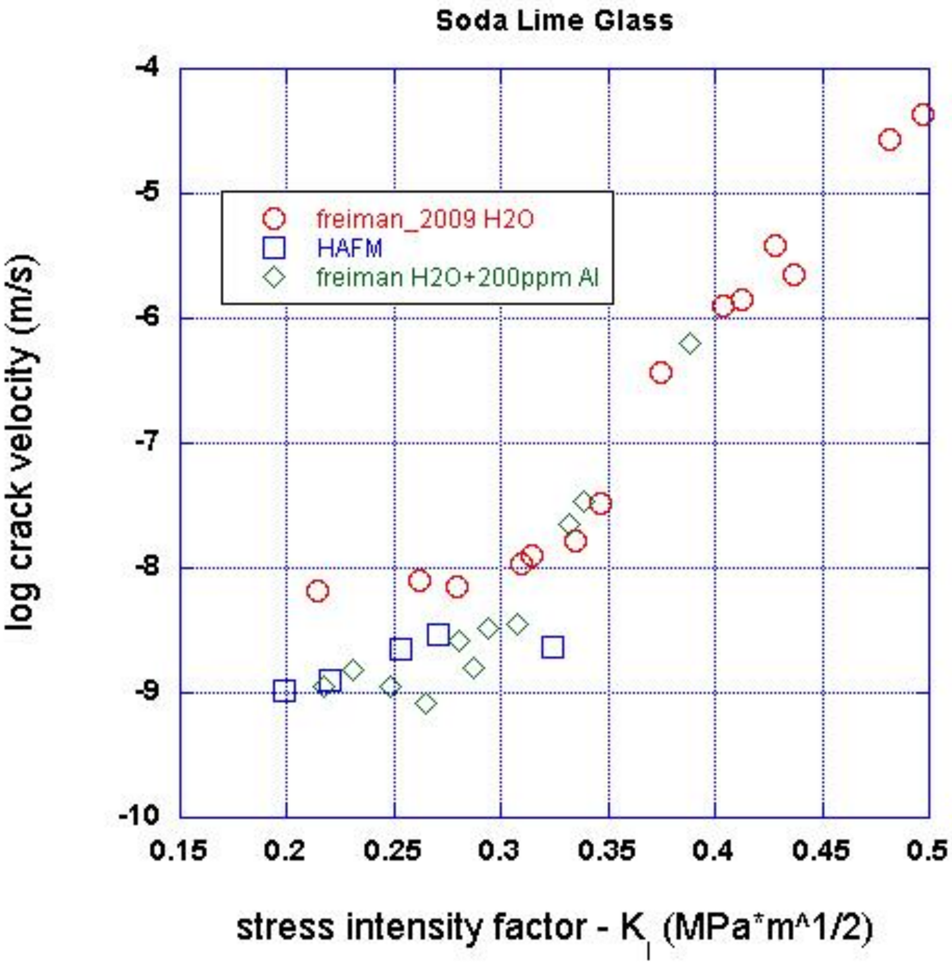
Experimentally accessible range with HAFM



S#13 ROC = 0.91 m K_i = 3.24x10^5 Pa*m$^{1/2}$

Conditions investigated:
T= 25 ºC; *P* = 2 bar; pH= 9.0 and *I*= 0.001 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

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Prepare samples, initiate cracks using Vickers Indenter, characterize glass using VSI, conduct SCG experiments as $f(K_i$, chemistry, T)	System assembled and tested, glass samples prepared, cracks initiated, conducted SCG experiments	Fall 2014
Complete glass SCG experiments, start quartz experiments, verify Dove model	Glass SCG experiments continue, novaculite has been obtained to test Dove model	In progress

Future Directions

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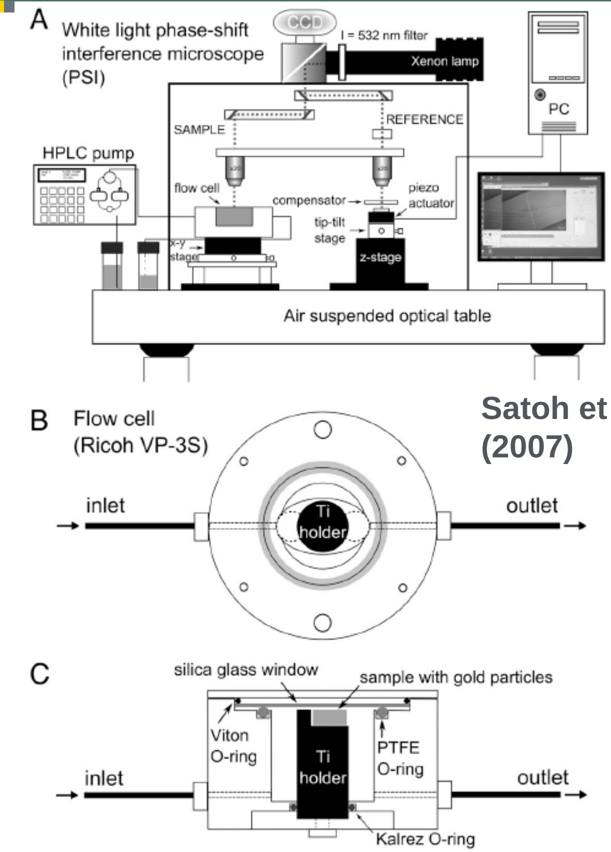
- Present research direction
  - Complete SCG experiments as proposed with glass as $f(K_i$, chemistry, T)
  - Continue SCG experiments as proposed with novaculite (quartz) as $f(K_i$, chemistry, T)
  - Verify that Dove (1995) Model is appropriate using quartz
  - HAFM-based crack velocity can be measured, 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



Satoh et al (2007)

Milestone or Go/No-Go FY15 remaining & FY16 (no-cost extension?)	Status and expected completion date
Prepare samples, initiate cracks using Vickers Indenter, characterize novaculite using VSI, conduct SCG experiments as $f(K_i$, chemistry, T) – verify Dove Model	Currently procuring novaculite (quartz), expect HAFM-based SCG experiments complete 10/15
Develop VSI/PSI-based SCG approach with French Soultz-sous-Forets collaborator	French project recently funded, initiating collaboration now

Mandatory Summary Slide

- We have successfully developed an HAFM-based approach to SCG velocity measurement
  - Crack velocity measured as $f(K_i$, 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-Forets geothermal site