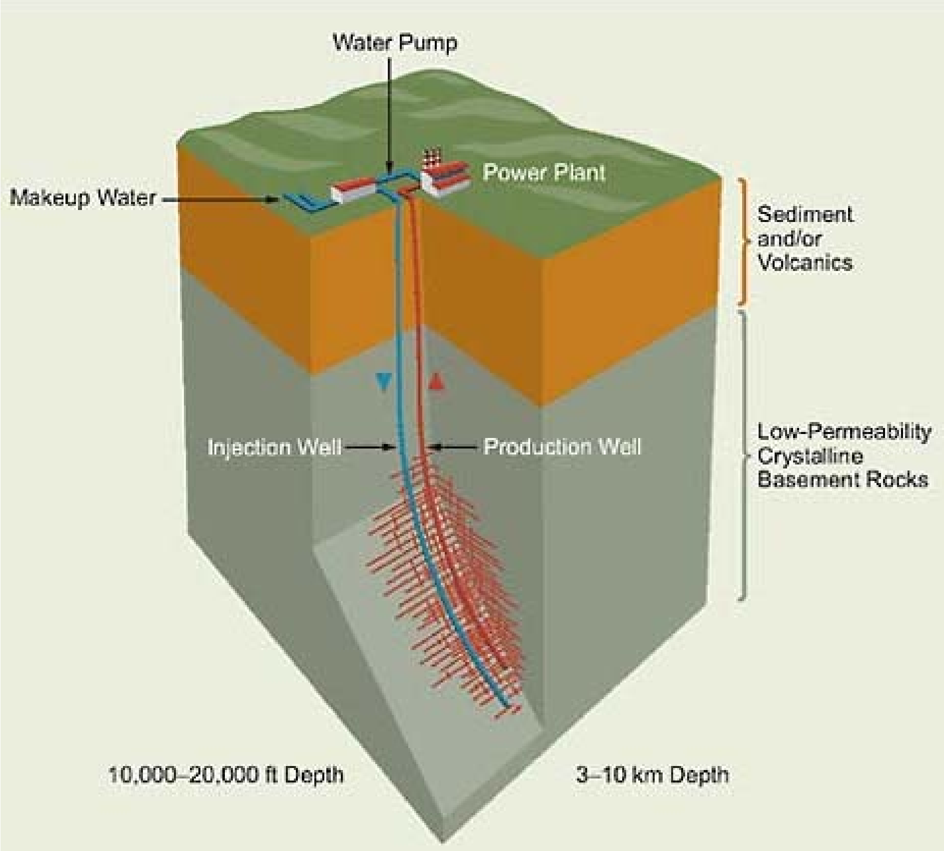
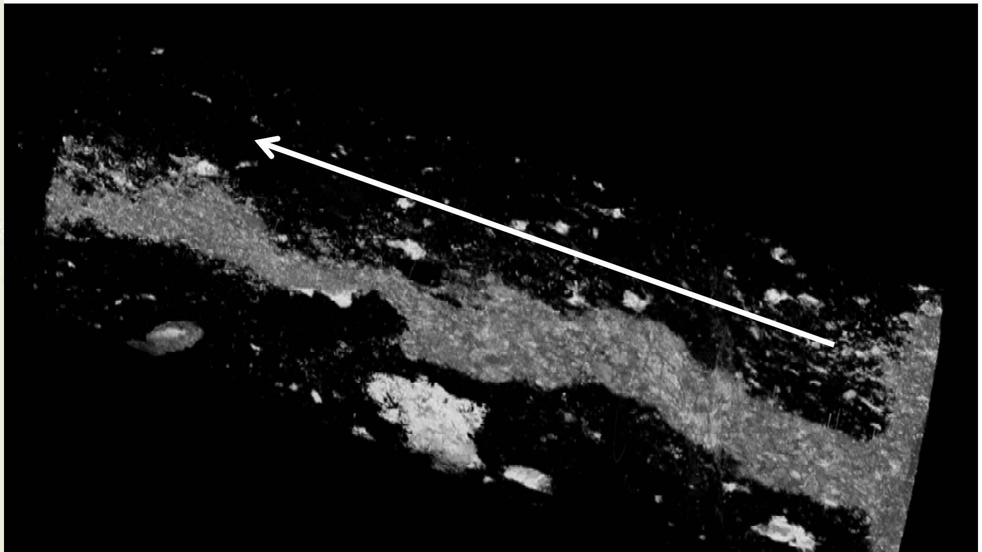


Impact of mineral reactions on shear zone permeability is uncertain at EGS conditions because key rate reactions are unknown



Increased fracture permeability after reaction with CO_2-brine at 200° C (Smith et al, 2013)

The Viability of Sustainable, Self-Propping Shear Zones in Enhanced Geothermal Systems: Measurement of Reaction Rates at Elevated Temperatures

Project Officer: Elisabet Metcalf; Total Project Funding: $900,000

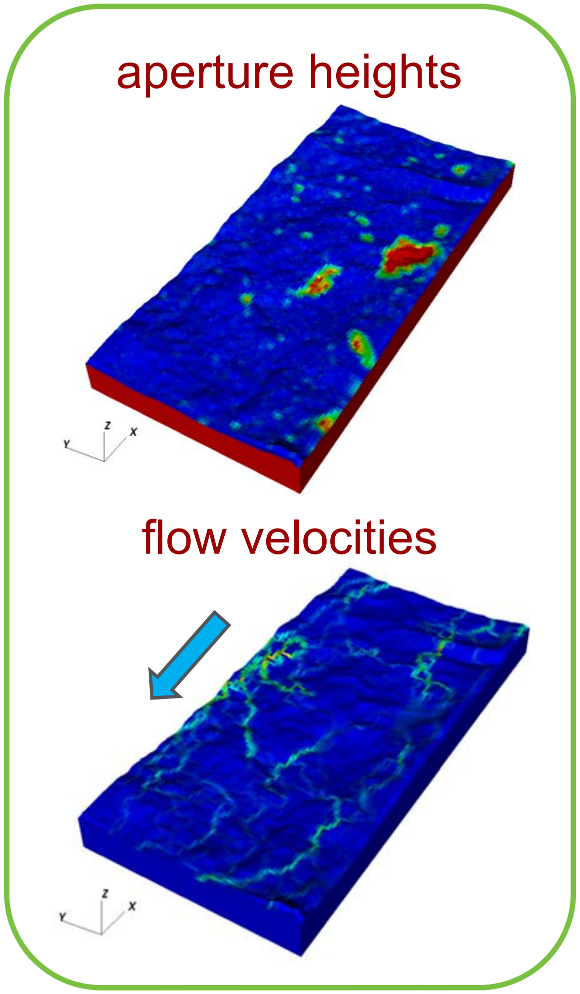
November 13-15, 2017

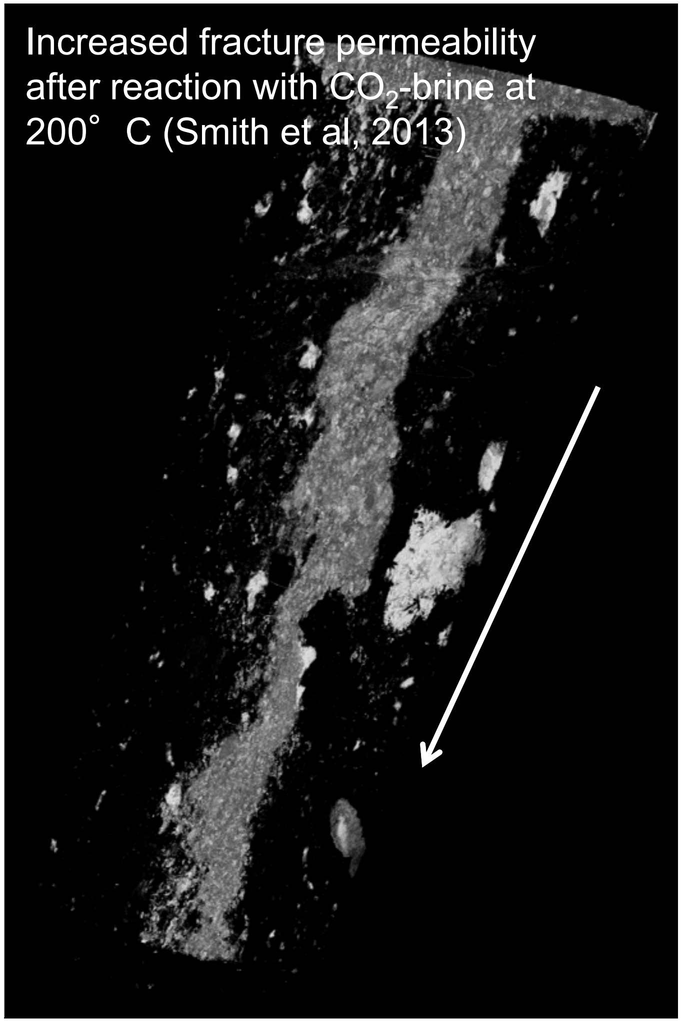
Susan Carroll, Megan Smith, Kristin Lammers
Lawrence Livermore National Laboratory

Track 3 - EGS Geoscience

Relevance/Impact of Research

- *GTO Need: Kinetic data are critical to designing and optimizing shear zone permeability for EGS systems.*





Relevance/Impact of Research

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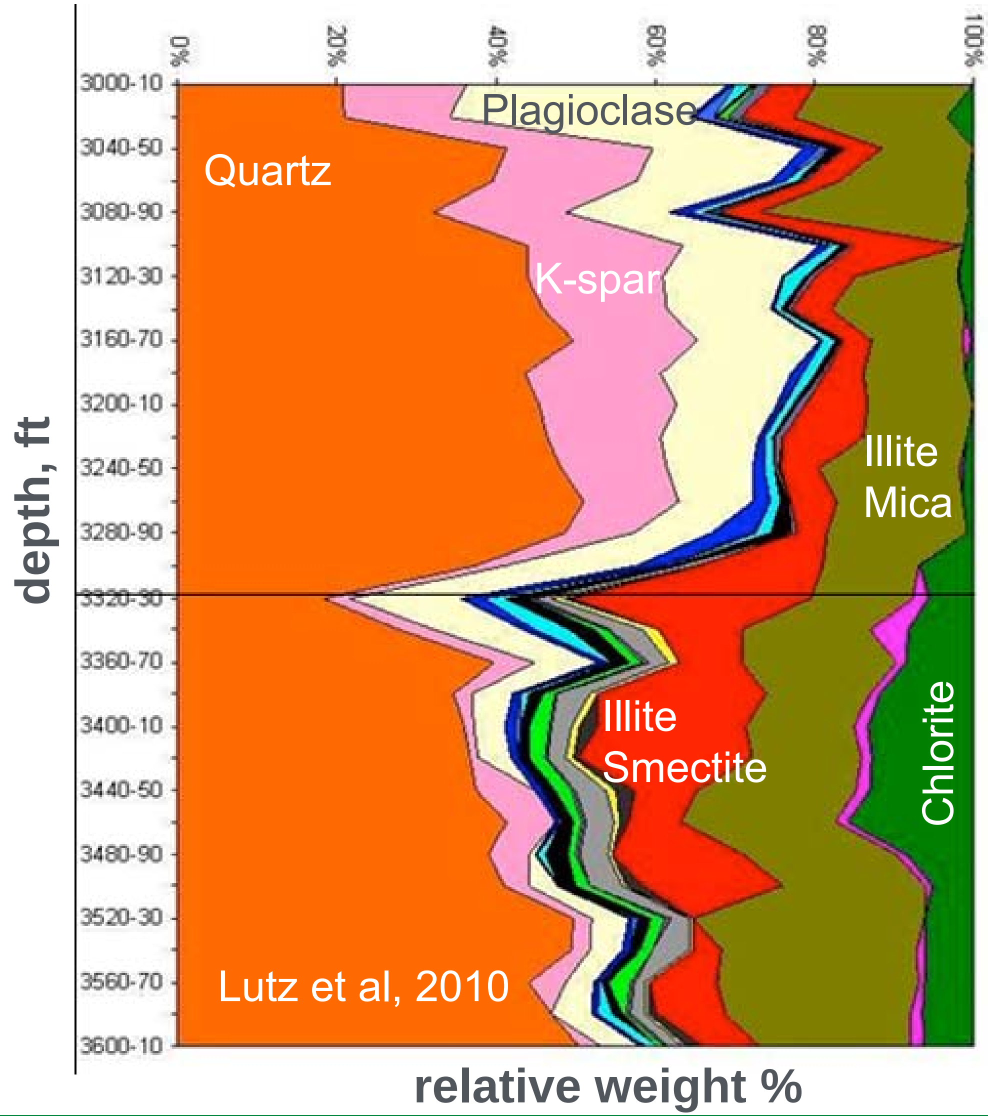
- **Kinetic Knowledge Gap Objective**
  - Expand geochemical kinetic database for fracture minerals identified in EGS shear stimulation zones to 300° C.

- **Current Technology Baseline Specifications**
  - Current kinetic data and rate equations are lacking for many shear zone minerals at EGS temperatures and are rare even to 100° C.

Shear Zone Minerals at Desert Peak



GTO Goal: Secure the Future with Enhanced Geothermal Systems

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- Results will allow chemical affects to be included in modeling, allow realistic estimates of risk from chemical reactions, and assist in designing economically viable EGS systems.

- Rate equation
  - Temperature
  - pH
  - Solution chemistry
  - Surface area

$$R\ (mol\ s^{-1}) = S\left(\left[A_A \cdot e^{-E_A/RT} \cdot a_{H^+}^{n}\right] + \left[A_N \cdot e^{-E_N/RT}\right] + \left[A_B \cdot e^{-E_B/RT} \cdot a_{OH^-}^{m}\right]\right) \cdot f(\Delta G_r)$$

  - New rate laws for 4 minerals (25 to 300C)
  - 111 new experiments + literature values

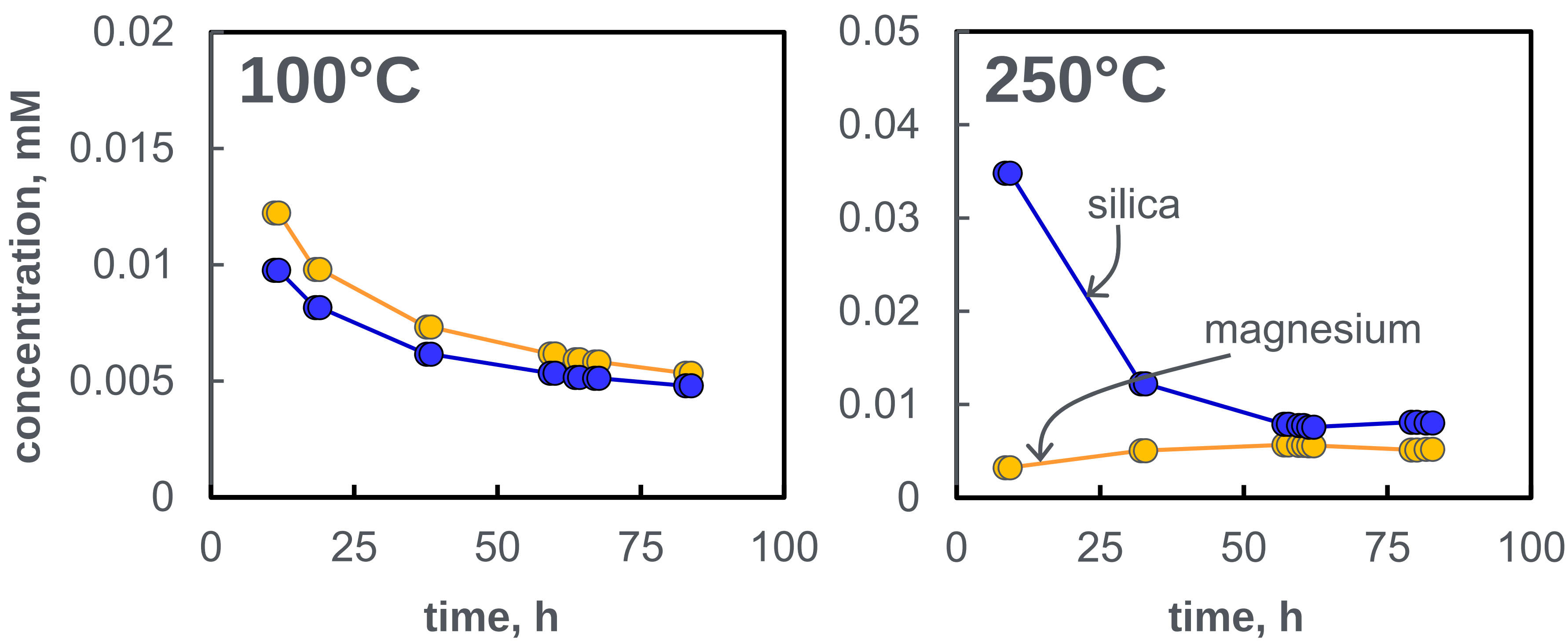
Scientific/Technical Tasks

- Detailed characterization of solids before and after reaction
  - TEM/SEM/XRD/BET
- Measure dissolution rates for shear zone minerals in mixed flow reactors
  - chlorite, illite, and biotite
  - pH 3 – 10
  - 100 - 300° C
  - $f(\Delta G_r)$
    - Desert Peak, Raft River, Bradys Hot Spring (~200° C)
    - Newberry (200-300° C)
- Derive dissolution rate equations to be used in reactive-transport simulations

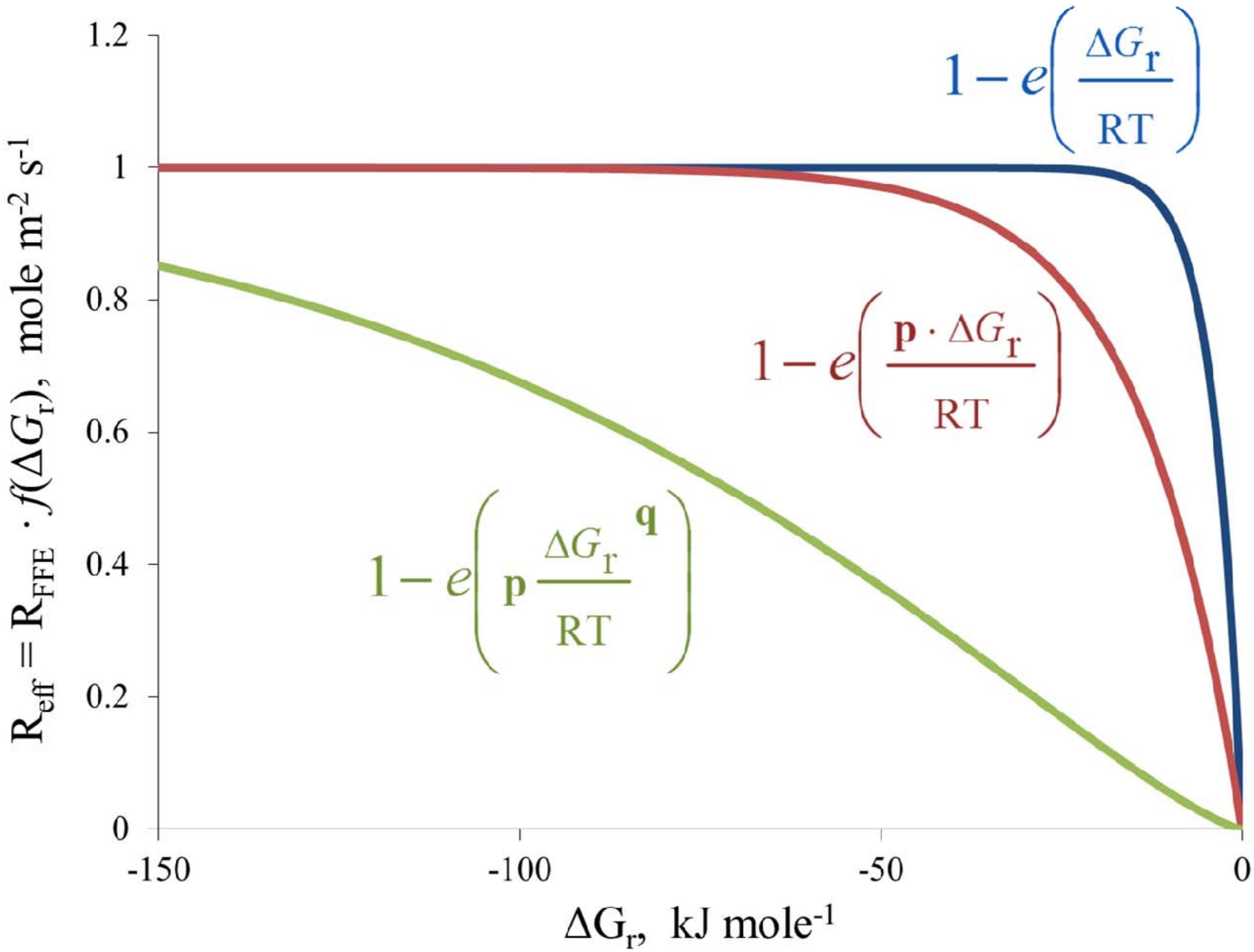
$$R\ (mol\ s^{-1}) = S\left(\begin{matrix}\left[A_A \cdot e^{-E_A/RT} \cdot a_{H^+}^{n}\right] + \left[A_N \cdot e^{-E_N/RT}\right] \\ + \left[A_B \cdot e^{-E_B/RT} \cdot a_{OH^-}^{m}\right]\end{matrix}\right) \cdot f(\Delta G_r)$$

Scientific/Technical Approach

- Rate ~ Δ [solution composition] x flow rate / surface area



Theoretical $f(\Delta G_r)$ terms slows rates only when the solution is very close to equilibrium



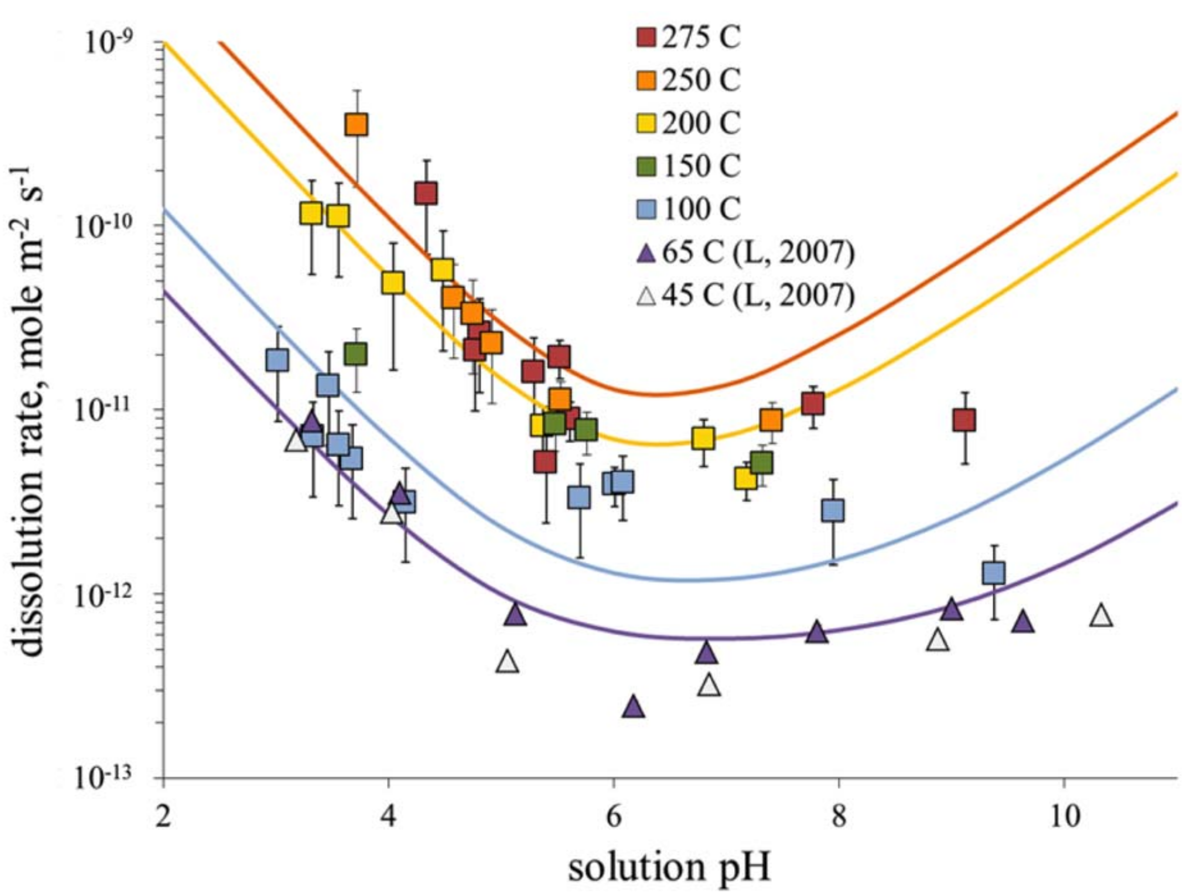
Summary: Rock-water interactions have the potential to alter shear zone permeability

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- Chlorite, biotite, illite, muscovite, and K feldspar are key fracture filling minerals in EGS shear zones
- Measured rates and derived equations so that they can be used to assess the role of geochemistry for EGS permeability using reactive transport codes.
- Illite, muscovite, feldspar are significantly more reactive than chlorite and biotite.
  - 100 to 1000 times faster
- The high reactivity of illite, muscovite, feldspar is likely to drive chemical alteration in shear zones. Rapid dissolution and secondary precipitation will likely impact flow and permeability in geothermal reservoirs.
- Peer-reviewed publication of new rate laws and with the Geothermal Data Repository

Chlorite $(Mg_{4.29}Al_{1.48}Fe_{0.10})(Al_{1.22}Si_{2.78})O_{10}(OH)_8$ Single rate equation from 25 to 275ºC

$$R_{Chlorite}\ (mole\ s^{-1}) = S\left(\left[5 \cdot 10^{-5} \cdot e^{-30.8/\mathrm{R \cdot T}} \cdot a_{H^+}^{0.65}\right] + \left[3 \cdot 10^{-10} \cdot e^{-18/\mathrm{R \cdot T}}\right] + \left[2 \cdot 10^{-7} \cdot e^{-26.3/\mathrm{R \cdot T}} \cdot a_{OH^-}^{0.43}\right]\right) \cdot \left(1 - e^{\Delta G_r/RT}\right)$$



Biotite $K_2(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4$ Single rate equation from 25 to 280°C

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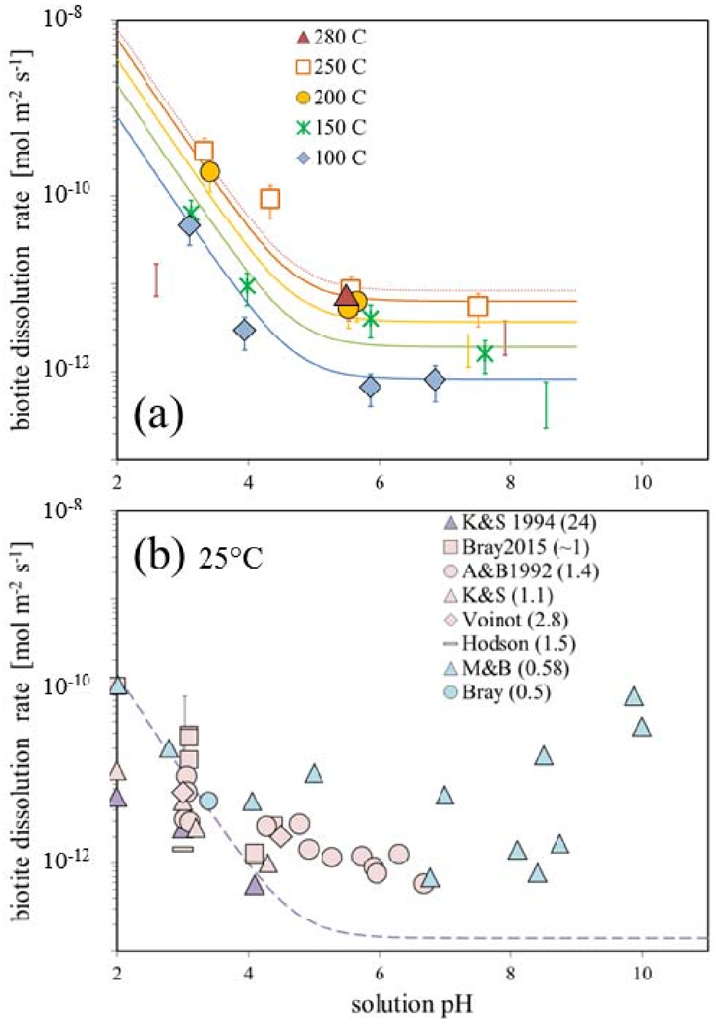

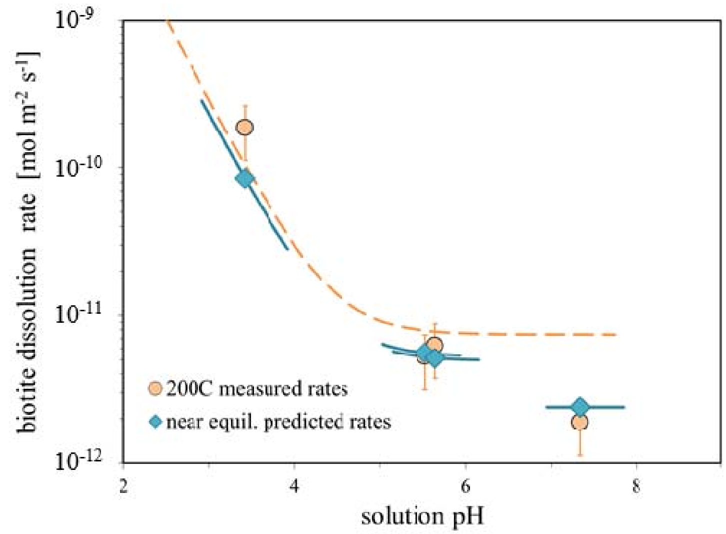

$$R_{biotite}\ (mole\ s^{-1}) = S\left(\left[1.5\cdot 10^{-4}\cdot e^{-22/\mathrm{R\cdot T}}\cdot a_{H^+}^{1.1}\right] + \left[10^{-9}\cdot e^{-22/\mathrm{R\cdot T}}\right]\right)\cdot\left(1-\left[e^{\Delta G_r/RT}\right]^{0.04}\right)$$

Illite $K_{1.55}(Na_{0.04},Ca_{0.02})Al_{2.90}(Fe_{0.70},Mg_{0.54},Ti_{0.05})Si_{6.75}Al_{1.25}O_{20}(OH)_4$
Single rate equation from 5 to 280ºC

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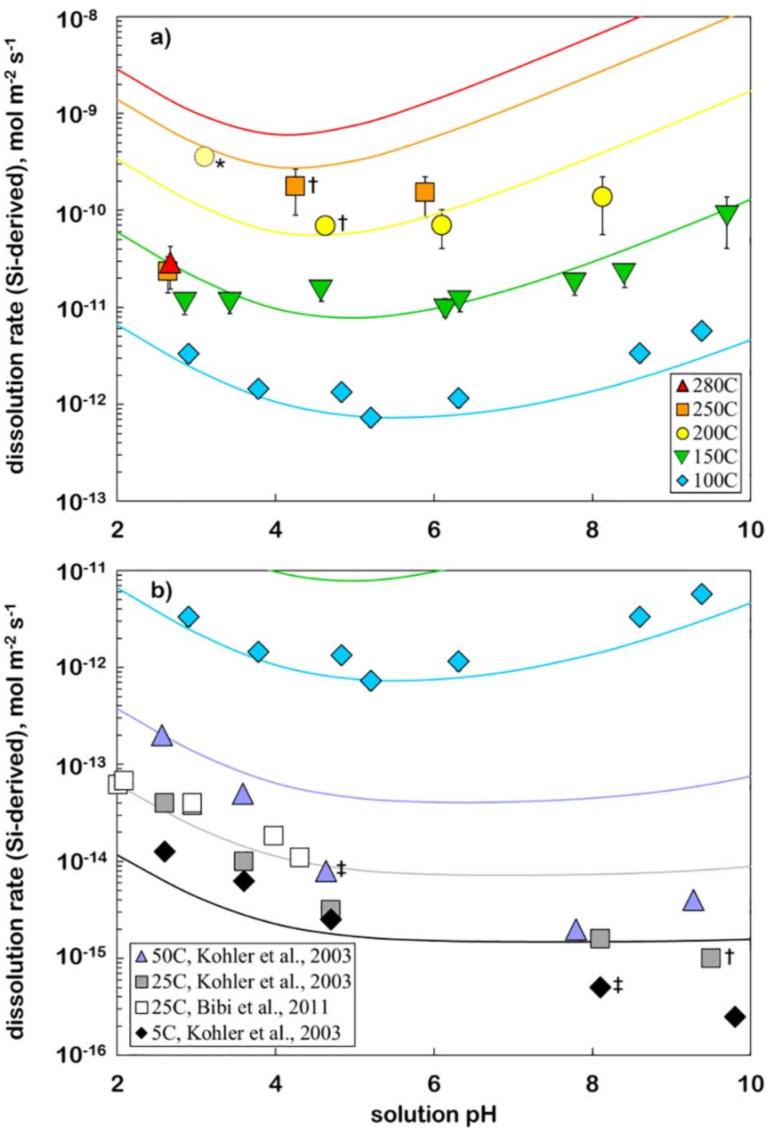
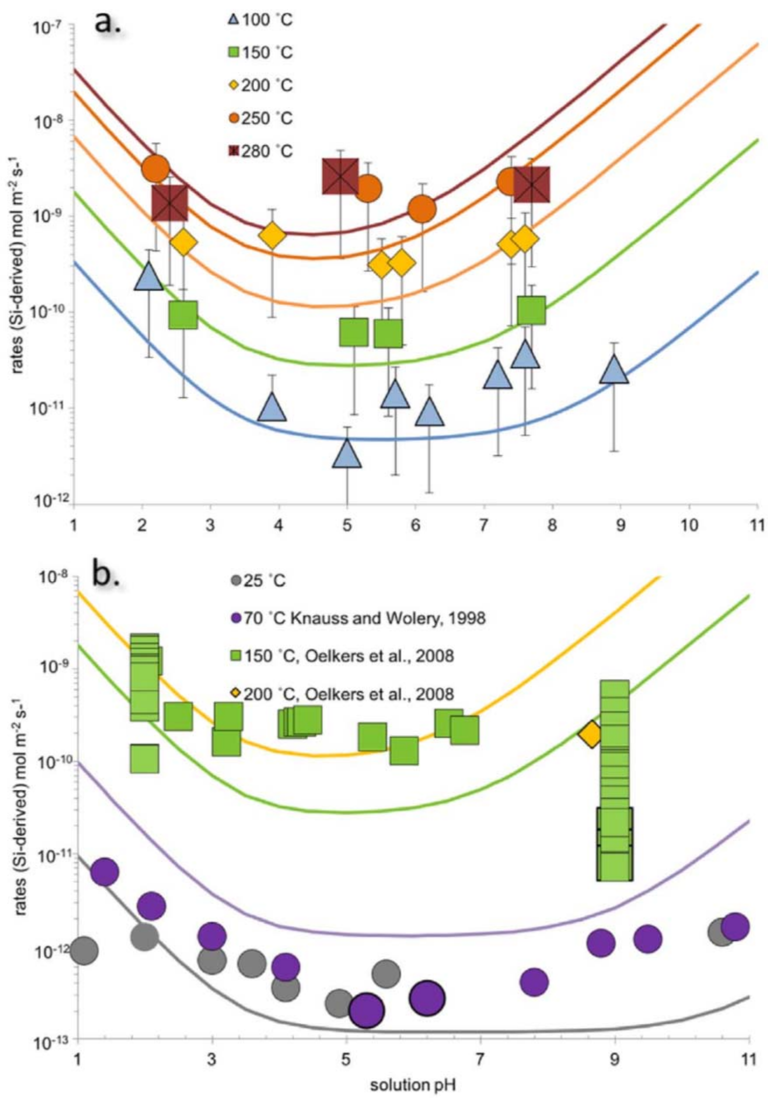


$$R_{illite}\ (mole\ s^{-1}) = S\left(\left[10^{-2}\cdot e^{-58/\mathrm{R\cdot T}}\cdot a_{H^+}^{0.55}\right] + \left[2\cdot 10^{-5}\cdot e^{-54/\mathrm{R\cdot T}}\right] + \left[10^{-4}\cdot e^{-77/\mathrm{R\cdot T}}\cdot a_{OH^-}^{0.35}\right]\right)\cdot\left(1-e^{\Delta G_r/RT}\right)$$

Muscovite $K_2(Al,Mg,Fe)_4(Si,Al)_6O_{20}(OH)_4$ Single rate equation from 5 to 280ºC



$$R_{muscovite}\ (mole\ s^{-1}) = S\left(\left[10^{-2}\cdot e^{-58/R\cdot T}\cdot a_{H^+}^{0.55}\right] + \left[2\cdot 10^{-5}\cdot e^{-54/R\cdot T}\right] + \left[10^{-4}\cdot e^{-77/R\cdot T}\cdot a_{OH^-}^{0.35}\right]\right)\cdot\left(1-e^{-\Delta G_r/RT}\right)$$

K-Feldspar: Working on a rate equation that accounts for reaction affinity

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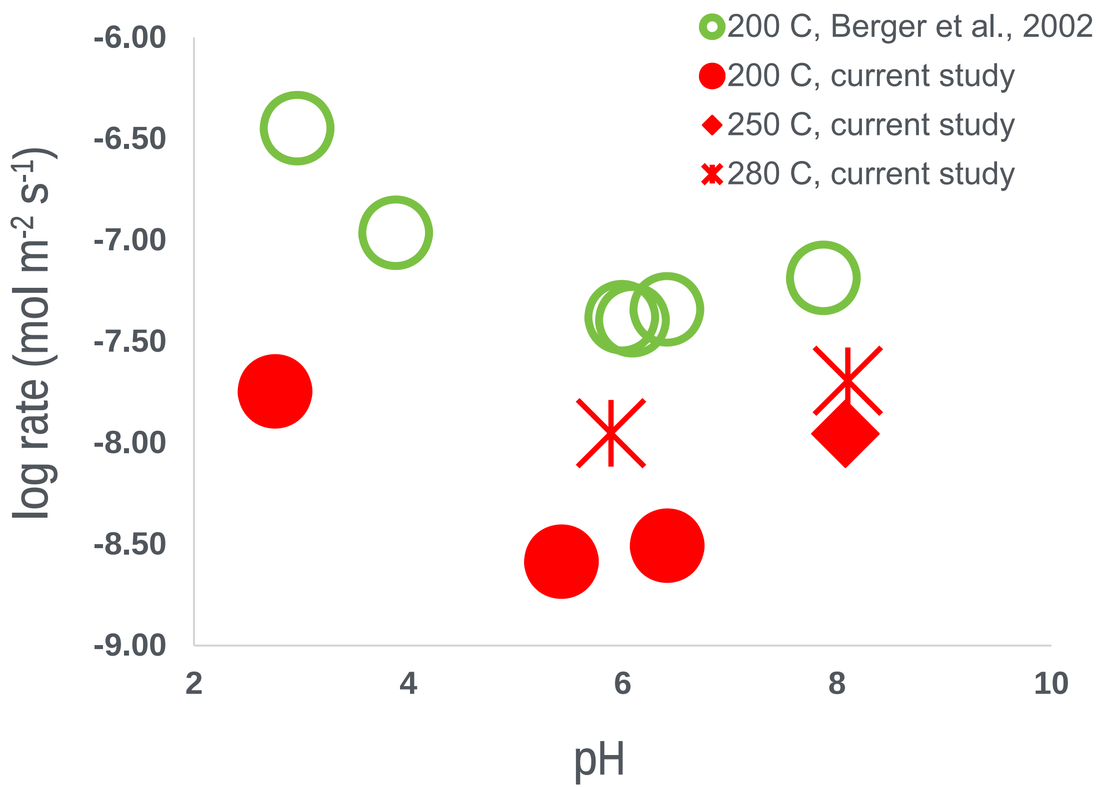
$$R_{K-spar}\ (mol\ s^{-1}) = S\left(\left[0.9 \cdot e^{-54/RT} \cdot a_{H^+}^{0.3}\right] + \left[6 \cdot 10^{-3} \cdot e^{-50/RT}\right] + \left[0.7 \cdot e^{-50/RT} \cdot a_{OH^-}^{0.3}\right]\right) \cdot \left(1 - e^{-4.9 \cdot 10^{-5}(\Delta G_r/RT)^{3.4}}\right)$$



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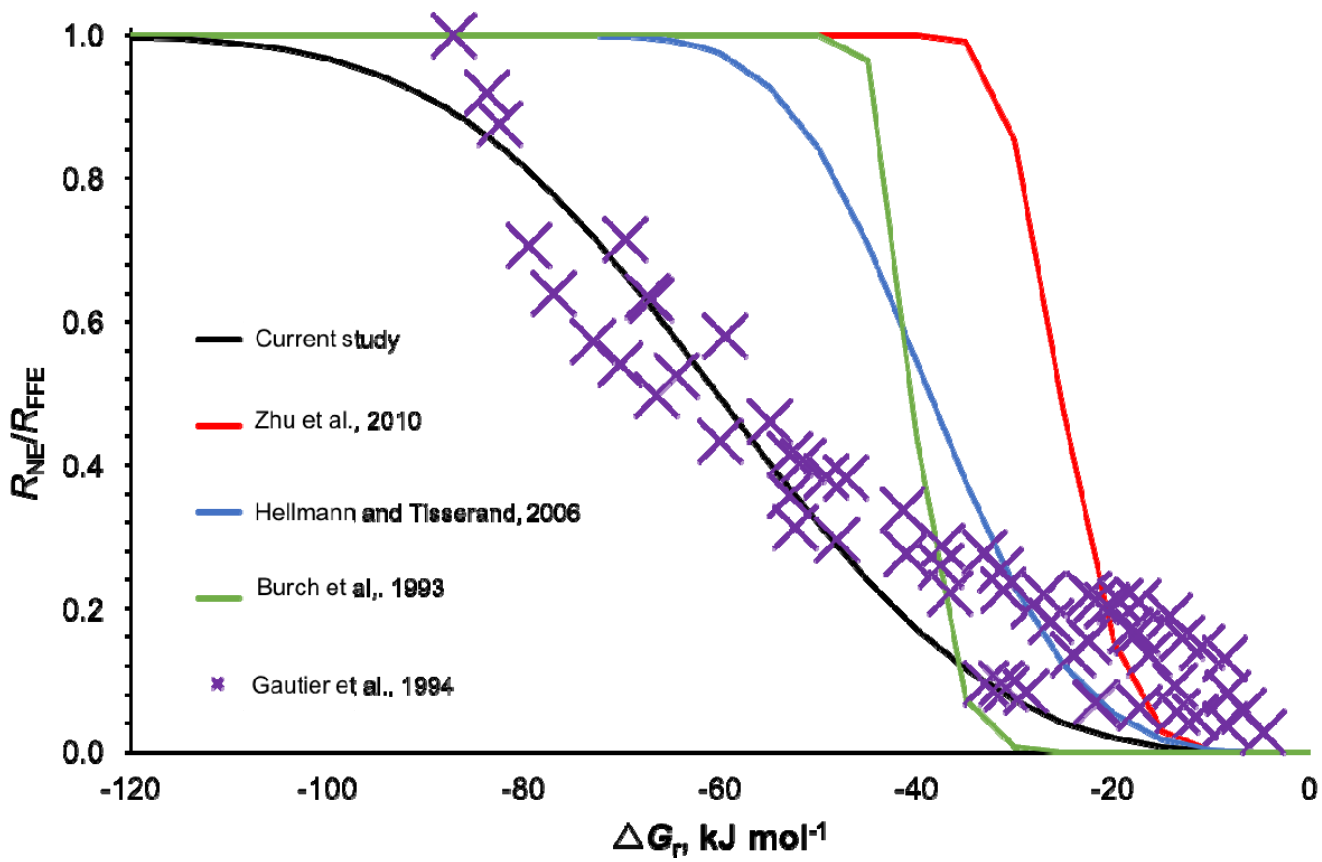

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Accomplishments, Results and Progress

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Status

- Complete

Deliverable

- Final report documenting updated EGS mineral kinetic database (2/15/2017)

Publications

- Smith, M. M., Carroll, S. A. (2017) Biotite dissolution kinetics at temperatures above 100 ° C, *Chemical Geology* (in revision)
- Lammers, K. Smith, M. M., Carroll, S. A. (2017) Muscovite dissolution kinetics as a function of pH at elevated temperature. *Chemical Geology,* https://doi.org/10.1016/j.chemgeo.2017.06.003
- Smith M., Dai, Z., Carroll, S. (2017) Illite dissolution kinetics from 100 to 280 ° C and pH 3 to 9. *Geochimica et Cosmochimica Acta*, 209, 9-23, http://dx.doi.org/10.1016/j.gca.2017.04.005
- Smith, M. M., Carroll, S. A. (2016) Chlorite dissolution kinetics at pH 3 – 10 and temperatures to 275° C, *Chemical Geology,* 421, 55-64, http://dx.doi.org/10.1016/j.chemgeo.2015.11.022

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