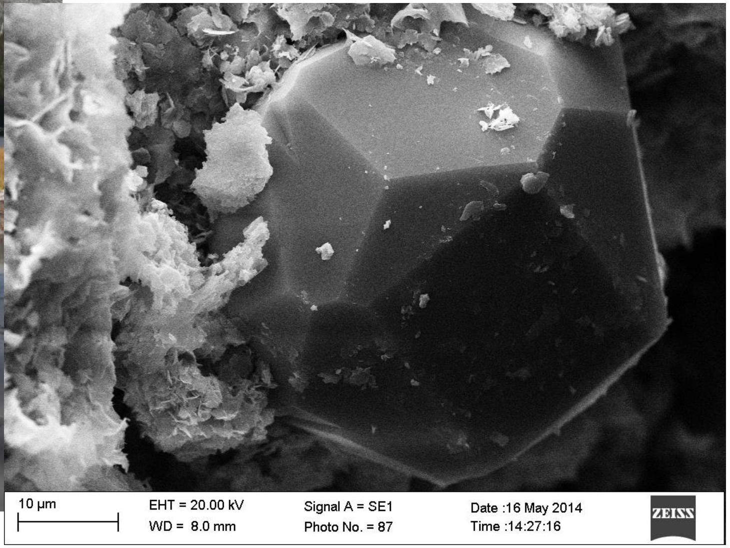
Newberry Volcano EGS

Desert Peak Rhyolite Experiment



Integration of Nontraditional Isotopic Systems Into Reaction-Transport Models of EGS For Exploration, Evaluation of Water-Rock Interaction, and Impacts of Water Chemistry on Reservoir Sustainability

Project Officer: Eric Hass

Total Project Funding: $138,255

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Track 2: Tracers / Zonal Isolation / Geochemistry

Relevance/Impact of Research

Objectives: Extend reaction transport models to incorporate standard and nontraditional isotopic systems used in EGS and validate methods with experimental work on reservoir rocks, and simulation of data from geothermal fields.

Challenges, barriers, knowledge gaps addressed:

1. *Design and development of improved geothermometers and geochemical tools to assist in discovering blind systems*
2. *Fluid rock interaction research to improve reservoir creation and reservoir sustainability*
3. *Understanding permeability using chemical signatures*
4. *Processing of different geochemical signatures to identify hidden geothermal systems*

Impacts to costs: Primary impacts on the costs are better constraints on reservoir rocks, depths and temperatures during resource exploration and better accuracy in determining the size and location of the geothermal resource. For EGS, the effective fracture surface areas can be much better constrained, leading to better stimulation planning and improvements in planning production well locations.

Impacts to following Geothermal Technologies Programs' goals:

EGS: Improved characterization of fracture surface area generated during stimulation (Ca, Sr, and Li). Improved predictions of fracture permeability changes from mineral precipitation to optimize production.
R&D: Coupled with THC models and aqueous geochemistry, isotopic systems are sensitive tools to evaluate the extent of fracture sealing or opening by dissolution (Ca and Sr for calcite, Li for clays).
Hydrothermal: Li isotopes sensitive to temperature and clay precipitation; Ca isotopic changes are sensitive to rates of calcite precipitation and sources; and Sr isotopes are strongly source-dependent – Quantitative analyses coupled with modeling will lower risks of exploration and improve resource evaluation.

Relevance/Impact of Research

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Despite widespread use of isotopic systems in evaluation/exploration of geothermal systems, few are incorporated into reaction-transport (RT) models that can allow for equilibrium and kinetic fractionation mechanisms.

Project Innovations:

Ca, Sr, and Li are commonly analyzed in geothermal waters for tracing water sources, mixing processes, and in geothermometry. A whole class of isotopic systems (e.g. Li, Ca, stable Sr) known as "nontraditional" can add to this range of processes (DePaolo 2006, 2011). *Ca, Sr, and Li isotopic systems incorporated into geothermal models for TOUGHREACT-V2 (Xu et al. 2011), V3-OMP (Sonnenthal et al., 2014) and -ROCMECH (Kim et al., 2012, 2015), extending the number and complexity of isotopic systems treated in reactive-transport models of geothermal systems.*

Common Ca and Sr-rich minerals in geothermal systems (feldspars, epidote, and calcite) often control fracture permeability changes. *Measurements of Ca and Sr isotopic fractionation at high temperature during calcite precipitation and alteration of reservoir rocks (e.g., Desert Peak rhyolite) have not been performed prior to this project, and will yield new data for determining fracture surface areas for heat transfer and water-rock interaction.*

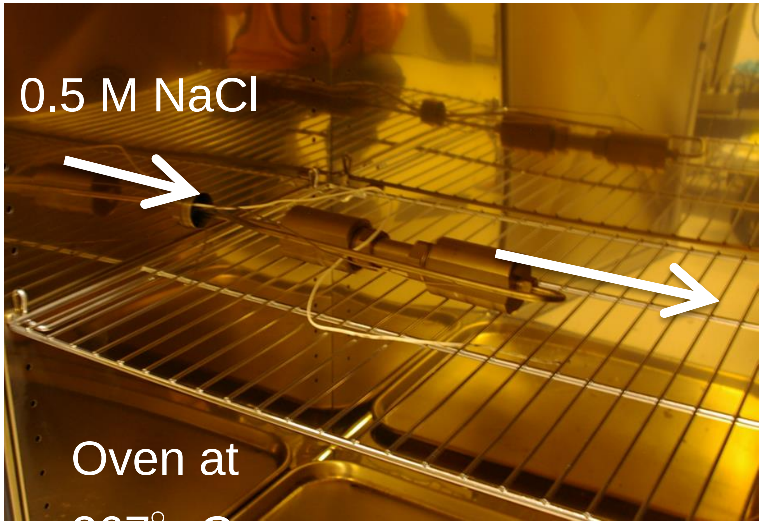
Lithium isotopes (^{7}Li and ^{6}Li) show strong mass- and T-dependent fractionation, making them a powerful tool for evaluating reservoir temperatures, and water-rock interaction (Millot and Negrel, 2007). *Determination of high-T fractionation factors and incorporation into THMC models will greatly add capabilities for analyzing EGS and hydrothermal systems.*

Scientific/Technical Approach

Team Members: John Christensen, Shaun Brown, Seiji Nakagawa, Christoph Wanner, Mack Kennedy (all at LBNL)

1. Integrate isotope systematics (i.e., Ca, Sr, and Li) into reactive-transport models of mineral-water-gas reactions in geothermal systems
2. Include dissolution, precipitation, sorption, ion exchange, and aqueous kinetics, kinetic and equilibrium isotopic fractionation
3. Design and build high P-T flow-through reactor
4. Run flow-through experiment over P-T-X conditions relevant for EGS and hydrothermal systems
5. Determine Ca, Sr, and Li isotopic compositions on samples over time
6. Analyze aqueous geochemistry and mineral reaction products
7. Develop and test THC models with isotope systematics on batch and flow-through experimental data
8. Evaluate parameters and models on data from field sites (Newberry EGS and Desert Peak)
9. Determine reactive surface areas and their evolution through coupled THC models and isotopic ratios

Flow-Through Reactor Experiment

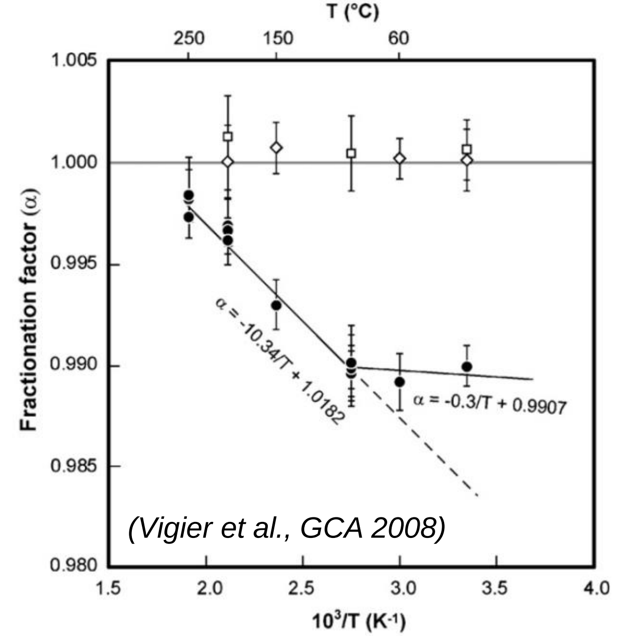


Scientific/Technical Approach

Li isotope systematics

- 2 stable Li isotopes: ^{6}Li (7.52%), ^{7}Li (92.48%)
- Substitutes with Mg^{2+} (similar ionic radii)
- Large potential for mass dependent isotope fractionation (17% mass difference), even at high temperatures
- Fractionation caused by Li incorporation during secondary mineral precipitation (e.g., clays)
- $\varepsilon = \delta^{7}Li_{2ndMin} - \delta^{7}Li_{solution}$ = -1.6‰ at T=250° C
- No or only little Li isotopic fractionation during dissolution of Li-bearing minerals

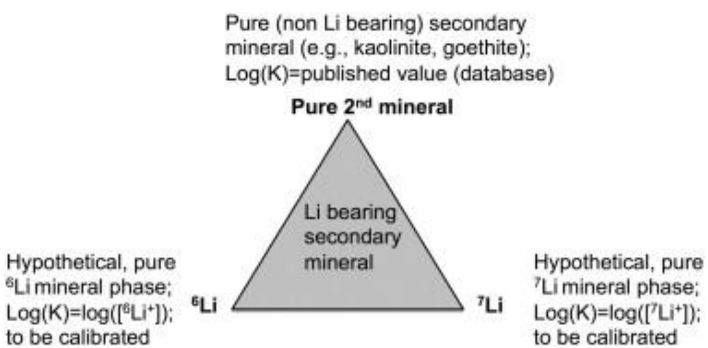
Fractionation by Li uptake in smectite



New Approach (Similar for Sr and Ca)

- ^{6}Li and ^{7}Li included in the mineral stoichiometry of Li-bearing minerals
- Fractionation simulated to occur exclusively during secondary mineral precipitation
- Li-bearing 2nd minerals simulated as solid solutions with 3 different end-members:

1. Pure (non Li-bearing) secondary mineral: Log(K)=published value
2. Hypothetical, pure ^{6}Li phase: Log(K)=log([6Li+]), calibrate
3. Hypothetical, pure ^{7}Li phase: Log(K)=log([7Li+]), calibrated



Wanner et al., Chem. Geol. 2014

Highlights

- A new rigorous thermodynamic-kinetic solid-solution formulation for THC modeling of Li ($^6Li/^7Li$) isotope fractionation during feldspar alteration to clays, as well as clay alteration, was developed.
- A high-temperature titanium flow-through reactor and geochemical sampling system was designed and used for a hydrothermal water-rock interaction experiment at reservoir temperature (267° C) and for time-scales similar to EGS experiments or significant flow through fault zones (~ 2 months)
- $^{87}Sr/^{86}Sr$, $^{44}Ca/^{40}Ca$ measured on flow-through reactor waters over time, along with aqueous chemistry and SEM/EDX
- The new parallel THC code (TOUGHREACT V3-OMP) with advances for modeling geothermal systems with isotope fractionation between water, gas, and minerals was used to simulate lab-scale and field-scale isotopic changes
- $^{87}Sr/^{86}Sr$, $^{44}Ca/^{40}Ca$ measured in flowback waters, along with $\delta^{18}O$ in H_2O-SO_4, δD, during the Newberry EGS 2014 stimulation, to evaluate fracture surface area and water-rock interaction temperatures

Accomplishments

- A new state-of-the art thermodynamic-kinetic formulation for modeling of Li (^{6}Li/^{7}Li) isotope fractionation during feldspar alteration to clays tracks the isotopic compositions in individual minerals and fluids, and published in Chemical Geology (Wanner et al., 2014).
- Ca and Sr isotopes have never been measured and modeled in a flow-through system under geothermal conditions with core samples from a geothermal reservoir (Desert Peak) and show strong systematic trends with reaction extent and time
- A full suite of water and gas analyses including Ca, Sr, O, H, and He isotopes have never been measured from a newly stimulated EGS system (Newberry Volcano)
- TOUGHREACT V3-OMP (Sonnenthal et al., 2014) was released through LBNL Tech Transfer

Keynote and Invited Presentations:

Sonnenthal, E.L., 2014. *TOUGHREACT: A Numerical Laboratory for Investigating Multiphase Flow and Reactive Transport in Geothermal Systems*. Keynote Presentation, New Zealand Geothermal Workshop, November, 2014.

Sonnenthal, E.L., 2014. *Multiple Continua, Isotopes, and Coupled Processes in Reactive Transport Modeling.* NSF Workshop on Reactive Transport, Alexandria, VA, April 13, 2014. Invited.

Sonnenthal, E.L., 2013. *Multicontinuum approach for modeling multiphase reactive geochemical and isotopic transport in geothermal systems*, in: AGU Fall Meeting Abstracts. p. 5. Invited.

Journal Publications:

Finsterle, S., Sonnenthal, E.L., Spycher, N., 2014. *Advances in subsurface modeling using the TOUGH suite of simulators.* Computers & Geosciences, 65, 2–12.

Wanner, C., L. Peiffer, E. Sonnenthal, N. Spycher, J. Iovenitti, and B.M. Kennedy, 2014. *Reactive transport modeling of the Dixie Valley geothermal area: Insights on flow and geothermometry.* Geothermics, 51:130-141.

Wanner, C., E.L. Sonnenthal, X-M Liu, 2014. *Seawater δ7Li: A direct proxy for global CO2 consumption by continental silicate weathering?* Chemical Geology, 381: 154-167.

Software Release:

Sonnenthal, E. L., Spycher, N., Xu, T., Zheng, L., Miller, N., Pruess, K., 2014. *TOUGHREACT V3.0-OMP*, http://esd.lbl.gov/research/projects/tough/software/toughreact.html.

Solid-Solution Model For Modeling Isotopic Reactive Transport

Overall precipitation rate:

$$r_{prec} = r_{pure2nd} + r_{^6Li} + r_{^7Li}$$

End-member precipitation rate:

$$r_{endm} = A \cdot k \cdot \left(1 - \frac{Q_{endm}}{K_{endm}}\right) + k \cdot A \cdot (x_{endm} - 1)$$

End-member mole fractions:

$$x_{^6Li} = \frac{Q_{^6Li}/K_{^6Li}}{Q_{^6Li}/K_{^6Li} + Q_{^7Li}/K_{^7Li}} \qquad x_{^7Li} = \frac{Q_{^7Li}/K_{^7Li}}{Q_{^6Li}/K_{^6Li} + Q_{^7Li}/K_{^7Li}}$$

Fractionation factor:

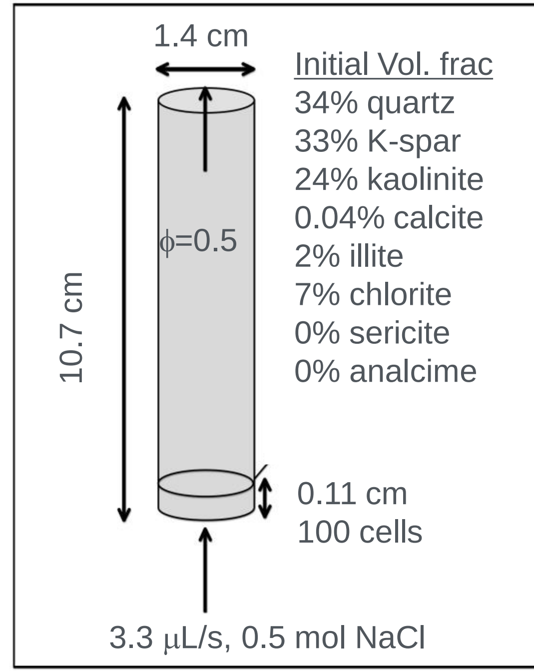
$$\alpha_{sim} = \frac{K_{^6Li}}{K_{^7Li}}$$

Wanner et al., Chem. Geol. 2014

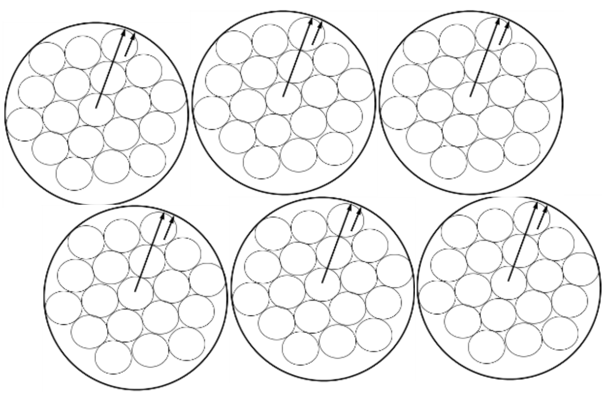
- 2 Li sources:
  - Illite: δ^7Li = -2‰ ($Mg_{-2}Li_{-1}Mg$)
  - K-feldspar: δ^7Li= +2‰ (K_{-1} Li)
- Li sink: formed sericite solid-solution
  - ε = -1.6‰ (Vigier et al., GCA 2008)

- Simulated as dual continuum model
  1. Bulk pore space: $k=10^{-13}$ m^2, 98.8% of total Φ
  2. Mineral surfaces: $k=10^{-20}$ m^2, 1.2% of total Φ
  - Diffusion+flow between the two domains

Model Set-up



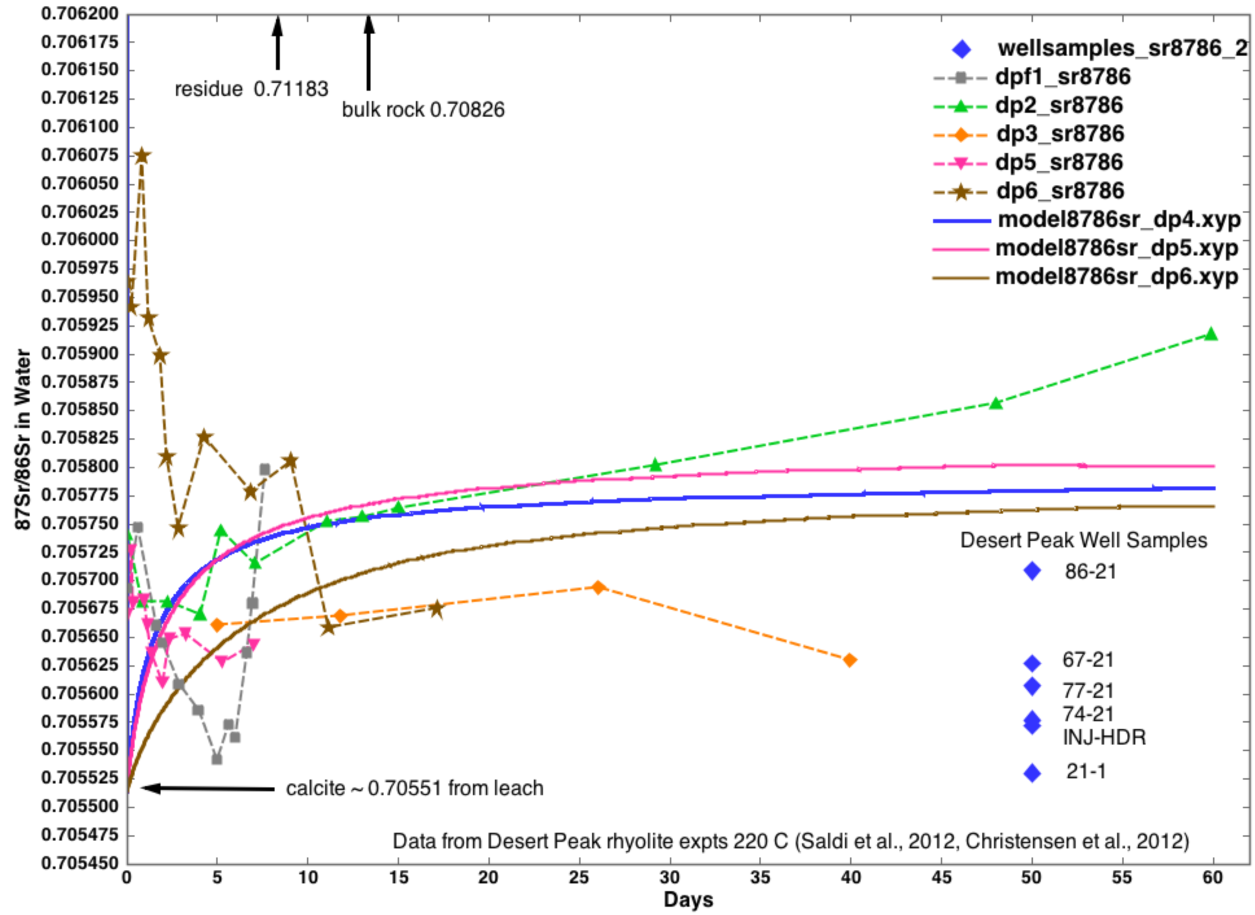
Dual-Continuum Model



Reactive Transport Model of Sr and Rb Isotopes For Desert Peak

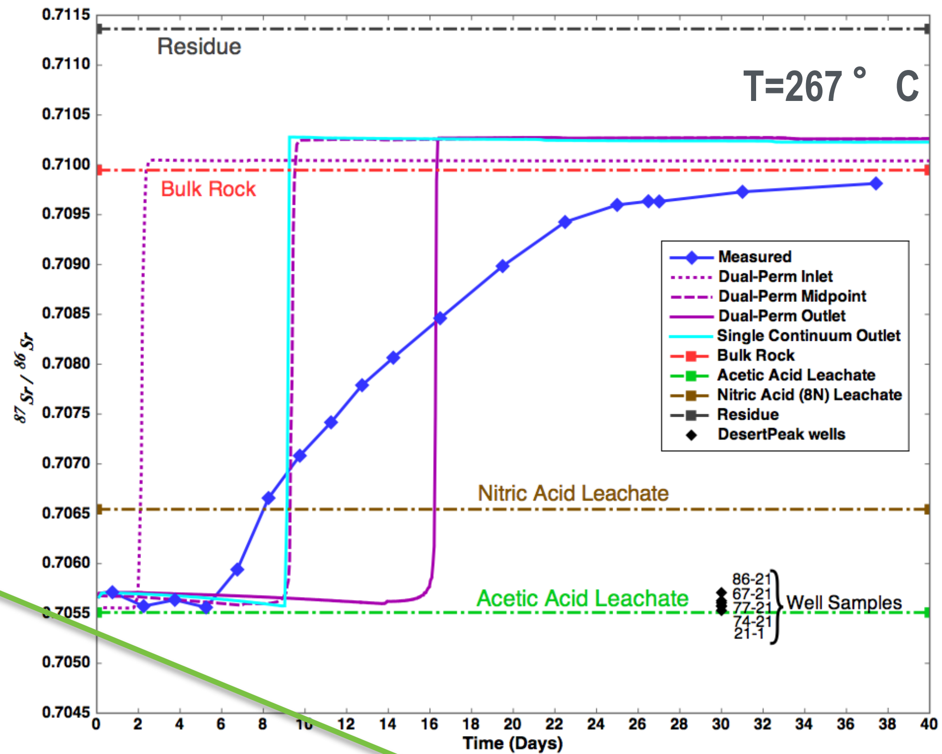
- Developed thermodynamic-kinetic reactive transport model for evolution of $^{87}Sr/^{86}Sr$ for water-rock reaction in complex hydrothermal mineral assemblages
- Simulated 220° C batch and flow-through experiments on Desert Peak altered rhyolitic ash flow tuff
- Simulations captured the overall trend in the isotopic ratios that is far lower than the bulk rock ratio
- Reaction of freshly crushed tuff shows somewhat higher values than well waters, which might be expected after EGS stimulation

Desert Peak Rhyolitic Tuff 220°C Reaction Experiments and Simulations



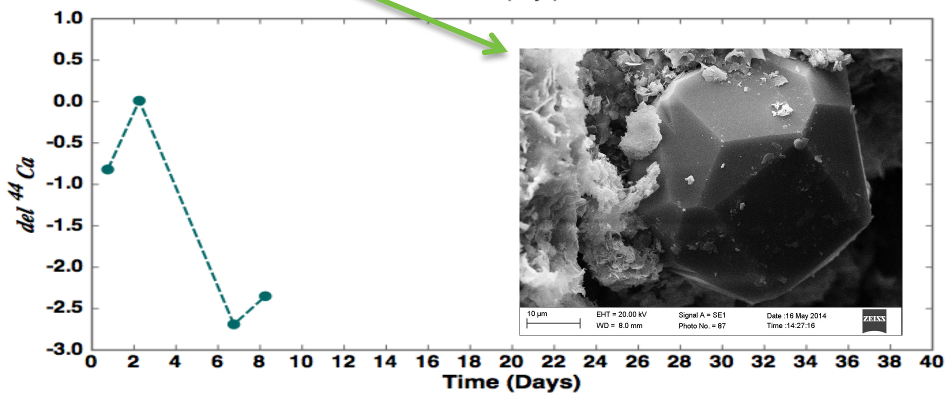
$^{87}Sr/^{86}Sr$ Results from Flow-Through Expt

- Samples from first 5 to 6 days show $^{87}Sr/^{86}Sr$ ratios slighly higher than acetic acid leachates -- calcite dissolution and desorbed Sr from clays
- Progressive trend toward bulk rock $^{87}Sr/^{86}Sr$ ratio from ~7 to 25 days, more than batch experiments
- Dual- and single-permeability models having $^{87}Sr/^{86}Sr$ in calcite of 0.7055 and 0.7113 in feldspar capture the early and late-time behavior but not the transition (surface areas of 1.3e4 to 1.3e5 m^2/m^3)
- Intermediate ratio silicate mineral or precipitation-redissolution along column may be responsible for the transition (analcime, micas seen in SEM)
- Samples from wells have ratios indicate isotopic equilibrium with secondary calcite
- Larger shifts to rock ratios more likely during EGS



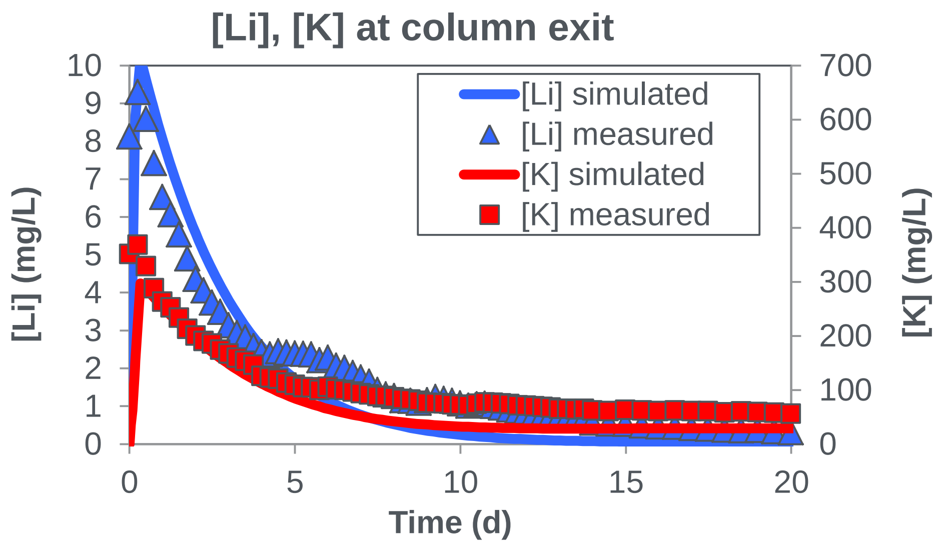
Preliminary $\delta^{44}Ca$ Results

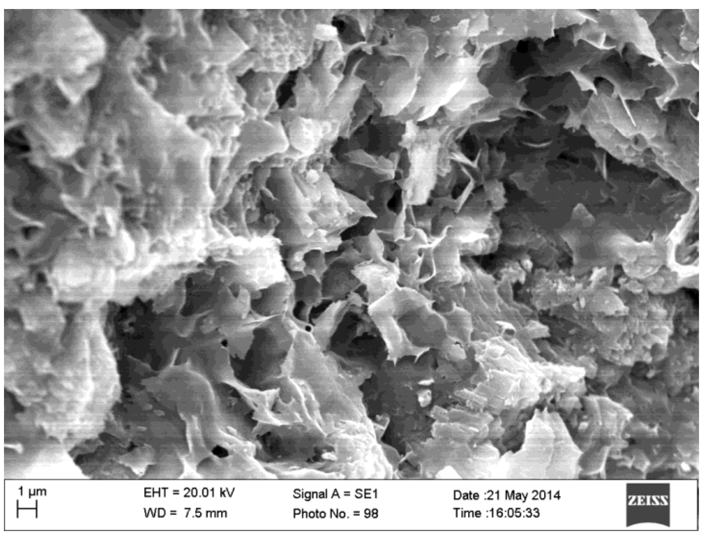
- Samples from first 2 days show slightly negative to near zero $\delta^{44}Ca$ values
- After ~7 days, $\delta^{44}Ca$ drops to strongly negative values, at the same time $^{87}Sr/^{86}Sr$ ratios are increasing
- Bulk rock and leachate analyses still needed for THC model initial conditions



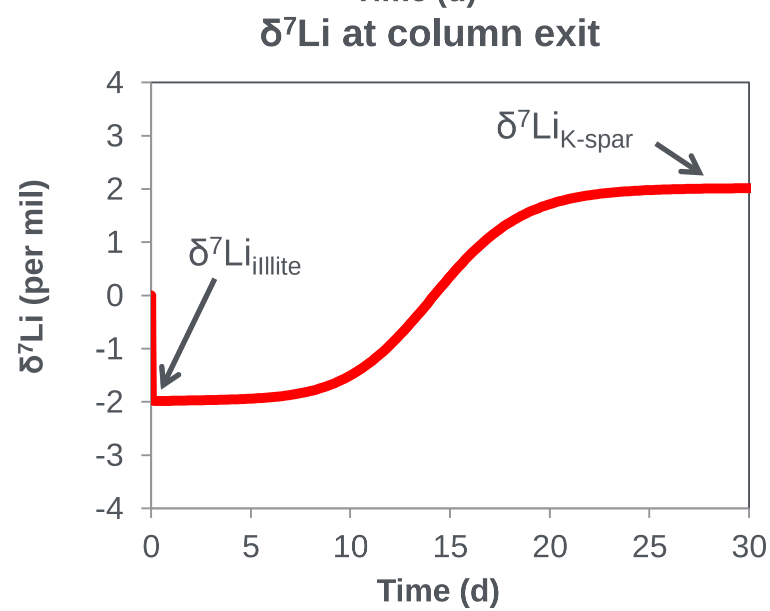
Cation Data/Model and δ^7Li Predictions

- Good model/data match for [Li] and [K]
- δ^7Li evolution strongly controlled by the two [Li] sources (illite vs. K-spar)
- Abundant sericite formed during experiment which should show similar effect as illite on δ^7Li
- Laboratory setbacks delayed δ^7Li analyses, but should be completed this FY



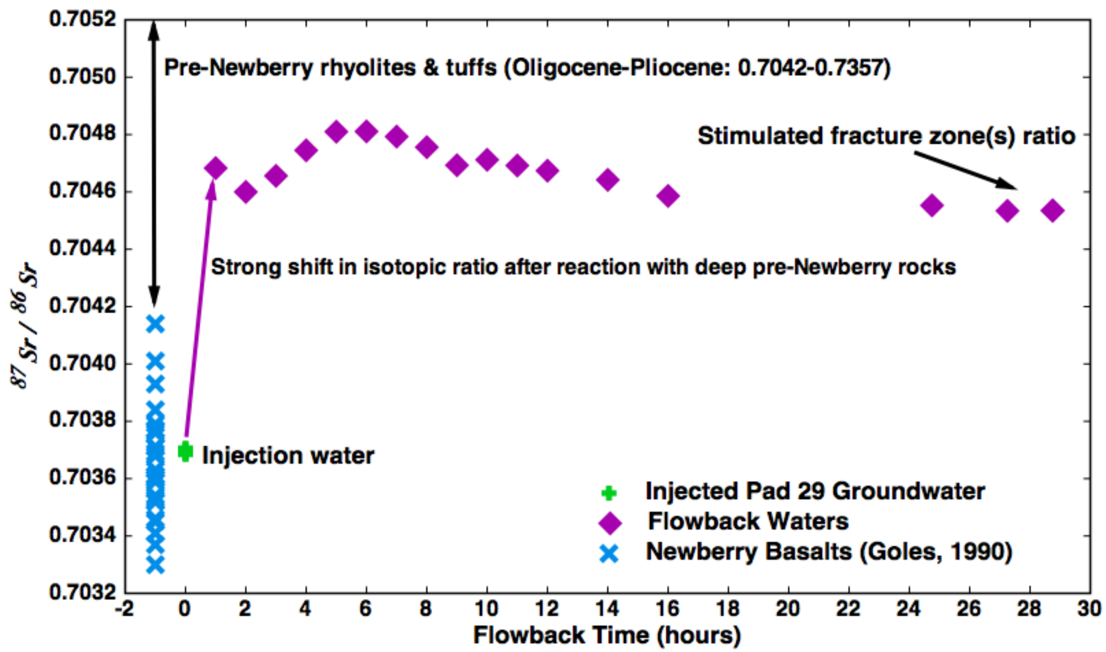


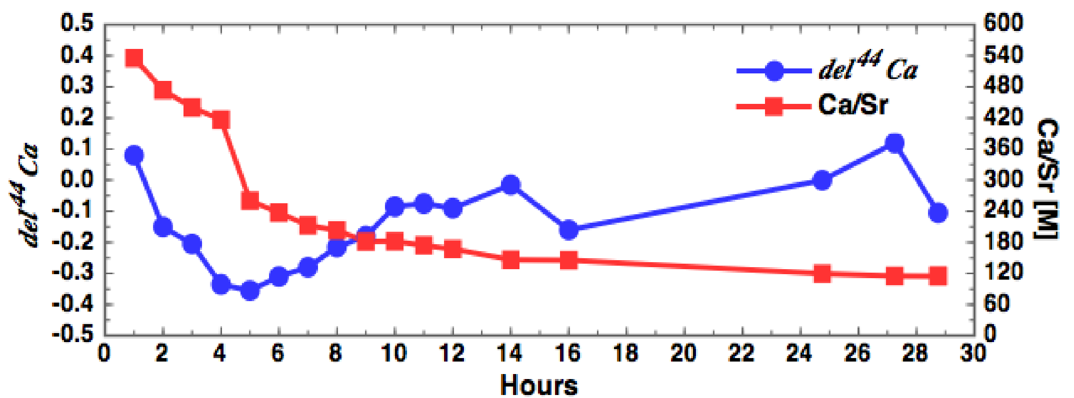
Sericite (i.e., mica): paragonite ($NaAl_2[(OH)_2AlSi_3O_{10}]$) – muscovite ($KAl_2[(OH)_2AlSi_3O_{10}]$) solid solution



Newberry Volcano EGS Sr & Ca Isotopes

- $^{87}Sr/^{86}Sr$ and $^{44}Ca/^{40}Ca$ measured on 1st set of flowback waters (after 3 week injection and 1 week shut-in period)
- Injected groundwater has $^{87}Sr/^{86}Sr$ ratio close to mean of all surface rocks
- Flowback waters show sharp increase to higher ratios only seen in much older pre-Newberry silicic rocks (e.g., Smith Rocks, Rattlesnake tuff)
- $\delta^{44}Ca$ values show trends related to calcite dissolution/precipitation
- Ca/Sr concentration ratios show a similar early drop suggesting calcite and silicate dissolution/precipitation
- *Isotopic ratios at later times should reflect rocks with higher Sr concentrations and reactivity in main stimulated fracture zones*
- Models are not well-constrained yet owing to unknown deep rock Sr and Ca isotopic ratios
- Will need to measure isotopic ratios in chip samples from deep volcanic and intrusive rocks





Accomplishments, Results and Progress

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Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
1.1 Develop thermodynamic and kinetic data	Sr & Rb in Desert Peak rhyolite, Li isotopes in Newberry EGS	Completed for Sr & Li 8/2014; $\delta^{44}Ca$ underway
1.2 Implement models for kinetic isotopic fractionation into TOUGHREACT databases	Published paper on kinetic fractionation: Wanner & Sonnenthal (2013); Published paper on Li isotopic fractionation: Wanner et al., (2014)	completed for Sr, Li 8/2014 $\delta^{44}Ca$ underway
1.3 Model 87Sr/86Sr in prior batch experiments on Desert Peak tuff	Simulated and presented at 2015 Stanford Geothermal Workshop	6/2014
1.4 Develop 2-D THC model of Desert Peak	2-D dual permeability THC cross-section developed; partial addition of isotopic systems (Sr, Ca, He, Li)	THC model completed 6/2015, Isotopes ongoing
1.5 Build high-temperature flow-through reactor	Flow-through reactor with chemical sampler	9/30/2013
1.6 Sample preparation for flow-through experiment	Desert Peak tuff core crushed, sieved, packed	11/1/2013
1.7 Perform flow-through experiment	~ 7-week experiment performed	1/26/2014
1.8 Cation and trace element analyses on water samples	Analysed 130 samples + SEM/EDX on minerals	3/2014
1.9 Sr, Ca, Li isotopes on water samples	Sr isotopes completed; preliminary Ca isotopes	Sr: 8/2014; Ca: 4/2015
2.0 Simulation of Newberry isotopic effects. Go-No go	Stimulation and flowback at Newberry Volcano in 2014 was successful (Go)	Sr and Ca isotope measurements completed 3/2015; Models being set-up

Future Directions

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- Outcome of this work will be a tested and published deployment strategy, reactive-transport code, and databases to simulate coupled THC processes and isotopes (Sr, Ca, Li) for constraining hydrothermal exploration models and EGS development/sustainability THMC models
- Research in FY2015 will include:
  - Analyses of Newberry EGS reservoir rock samples for constraining inputs to THMC-isotope models
  - Simulation of Newberry EGS to constrain permeability changes, fracture surface area and zones, coupled to temperature and flow measurements, flowback water and gas chemistry and geothermometry
  - Simulations of Desert Peak Sr, Ca, and Li isotopes coupled to 3He/4He (another AOP project)
  - Only remaining issue is the acquisition of Li isotopes, which require improvements to separation
  - If funding permits, run flow-through experiment on Newberry EGS reservoir samples using same injected groundwater (late FY2015-FY2016?)

Milestone or Go/No-Go	Status & Expected Completion Date
Submit paper on Sr-Ca isotopes in Desert Peak flow-through experiment	Analyses/Modeling about 80% complete. 7/31/2015
Submit paper on Newberry EGS Sr-Ca Isotopes	Analyses/Modeling about 60% complete. 8/30/2015
Perform Li Isotopes on Desert Peak samples (Go-No Go). If not successful, then look into sending to outside lab	Not done yet. Anticipated by 6/30/2015
Submit paper on Sr isotopes coupled to Desert Peak 2-D THC Model with constraints on fault permeabilities	Modeling about 70% complete. May need some additional field samples. 9/30/2015
Flow-through experiment on Newberry reservoir samples. Go-NoGO depends on funding/continuation in FY2016.	Not initially in plan, but would yield greatest impact on EGS project to constrain stimulated fracture volume/area. 12/2015?

Summary

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- A flow-through experiment on a geothermal reservoir rock from Desert Peak show strong shifts in Sr and Ca isotopic ratios that reflect desorption from clays, calcite dissolution, and finally feldspar reactions, to a much greater extent than in previous batch experiments
- A new thermodynamic-kinetic solid solution model was developed to incorporate more detailed Li, Sr, and Ca isotopic changes in THC models of water-rock interaction.
- Simulations using the newly released parallel THC code TOUGHREACT V3-OMP capture the overall trend in Sr isotopic changes as a function of the reactive surface area, although some details of the intermediate reactions are still uncertain.
- Ca isotopes are more sensitive to calcite dissolution and rates of calcite precipitation. Preliminary values from the Desert Peak expt show a very strong shift in the isotopic ratio to highly negative values. Should provide a key constraint on reaction rates.
- Simulations of δ^7Li changes in the experiment, suggest that shifts in the ratio should be observable; however measurements delayed.
- Flowback waters from the Newberry Volcano EGS were collected in Oct. 2014 and analyzed for Sr and Ca isotopes.
- Strong shifts in the ^{87}Sr/^{86}Sr ratio to more radiogenic values than the groundwater or any rocks from Newberry Volcano, indicate reactions with pre-Newberry (possibly Oligocene-Pliocene) silicic volcanics that outcrop in central-eastern Oregon.
- Along with observed shifts in Ca isotopic ratios, and water and gas chemistry, will strongly constrain fracture surface areas, stimulated fracture zones, and permeability changes during EGS stimulation in THMC models