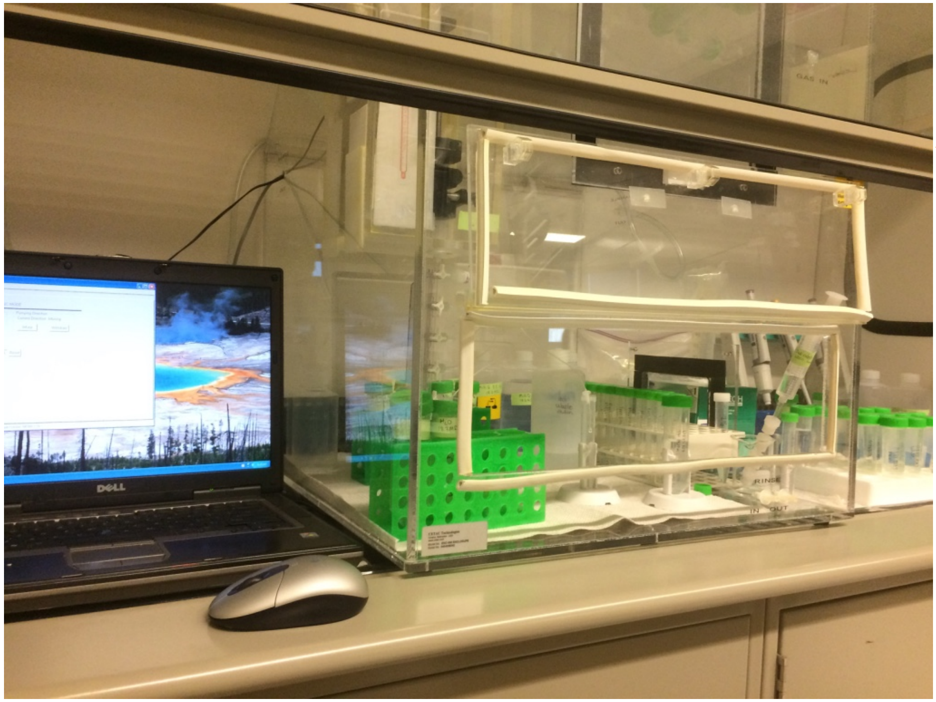

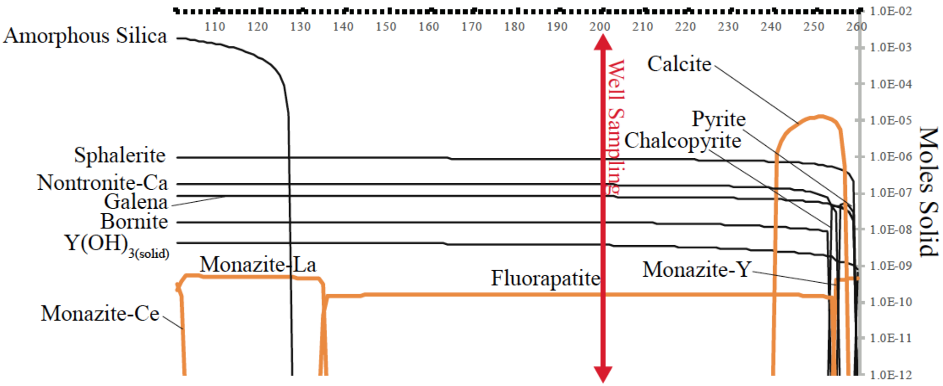

Maximizing REE Recovery in Geothermal Systems

Project Officer: Holly Thomas
Total Project Funding: $567307
November 15, 2017

Mandatory slide

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University of California Davis
University of Oregon

Track 1 – Mineral Recovery

Relevance to Industry Needs and GTO Objectives

Challenges, barriers, knowledge gaps, or problems being address by this project:

Quantify REE in various geothermal settings and develop predictive modeling capabilities

- Current data on REE concentrations in geothermal fluids are limited
- Controls on REE transport in geothermal fluids are poorly understood
- Current REE thermodynamic compilations are inadequate
- No versatile modeling software capable to making predictive aqueous REE models

Project impact to costs, performance, applications, markets, or other factors in geothermal energy development:

- Quantified the potential economic value of REE in geothermal fluids
- Improved knowledge of mass transfer in geothermal systems
- Geochemical characteristics of REE may be an innovative means to inform exploration and operation of geothermal resources and evaluate the success of EGS approaches.

Relevance to Industry Needs and GTO Objectives

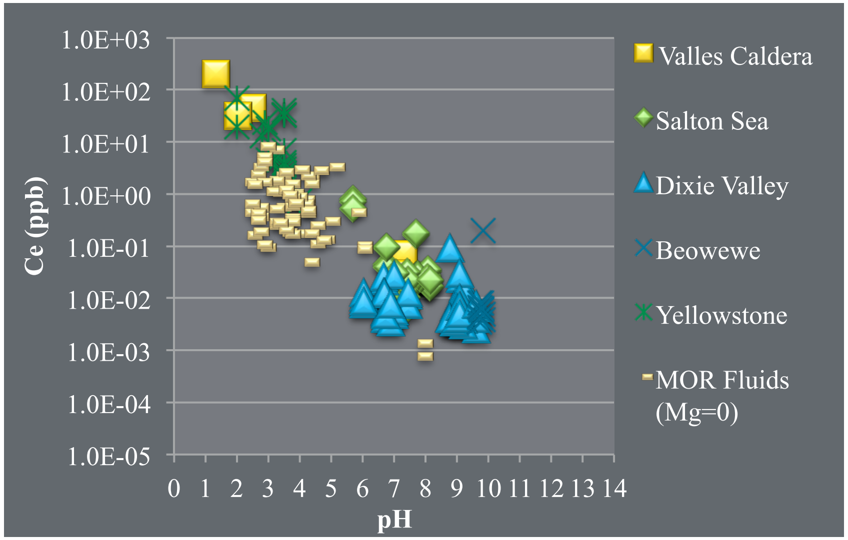
Innovative aspects of your project:

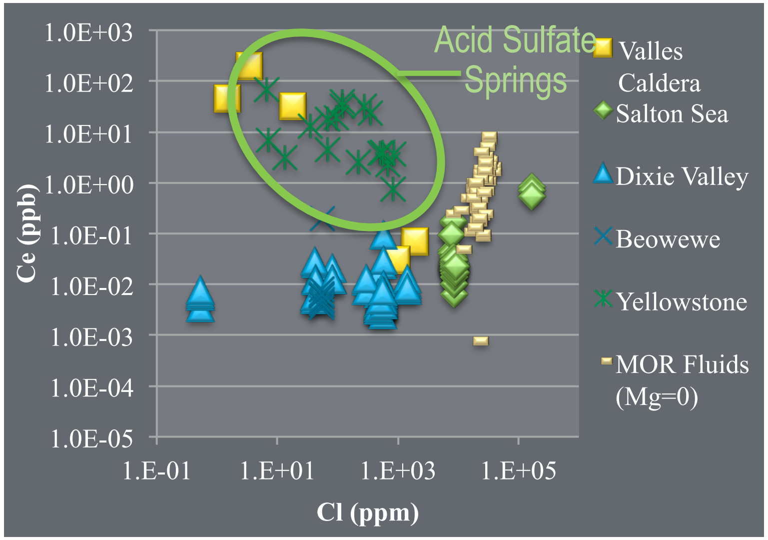
- Developed analytical techniques to measure picomole REE concentrations in 10 to 20 mL sample sizes
- Provided analytical data for geothermal fluids with range of compositions for which data were not previously available
- Produced a compilation of the most current thermochemical data for use in versatile geochemical modeling software
- Determined important controls on REE transport in geothermal fluids

How success within this project will impact the Geothermal Technologies Office's Goals

- Provided data allowing GTO to quantify the potential to reduce geothermal energy operating costs by recovery of REE from geothermal fluids.
- Consistent with studies in this program that suggested REE are not present in sufficient quantities in wellhead fluids to be a viable economic commodity.
- Our studies suggests REE are present in significantly higher concentrations in unboiled, down hole fluids; data not available to other studies.
- We will verify our model predictions by shortly collecting downhole fluid samples

Methods/Approach

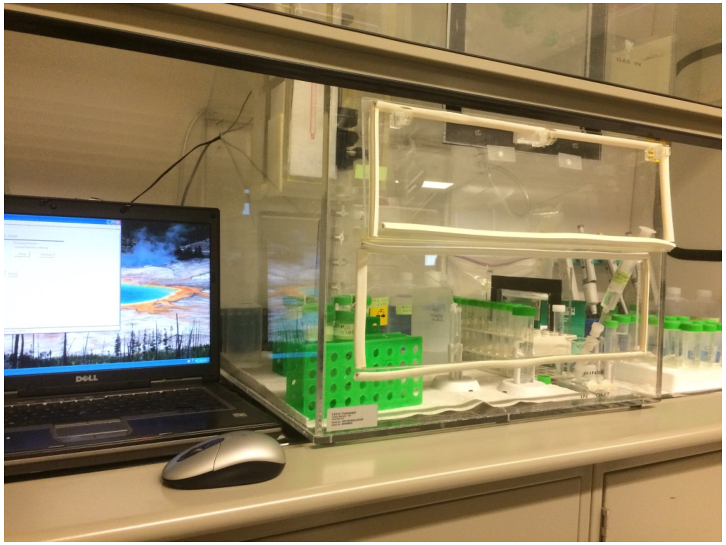




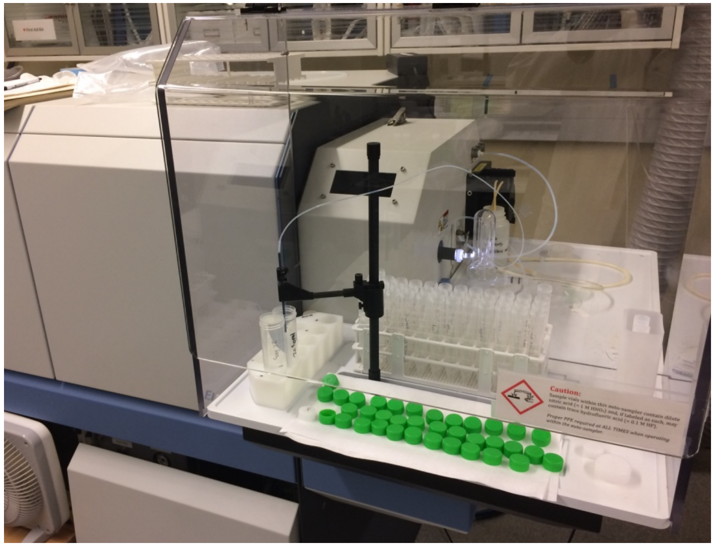
Approach: Compile and evaluate existing data to qualitatively identify geothermal fields with greatest likelihood of economically viable REE concentrations

- Temperature, Cl and pH appear to be most important controls on REE in geothermal/hydrothermal fluids.
- Compilation was made available to other DOE research teams and is publically available on GDR.

Methods/Approach



Apparatus developed based on modified version of Zhu et al. (2010) method for REE measurement



Thermo Scientific Element XR Magnetic Sector ICP-MS

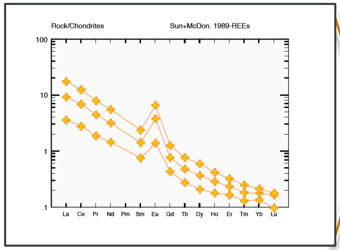
- REE Data not available for many geothermal locations, and available analytical methods required large sample volumes, expensive reagents, and have high detection limits.
- We developed an offline preconcentration analytical method to analyze picomolar REE concentrations in saline geothermal fluids.
- Nominally 1 ppt detection limit for most REE on 10-20 ml sample sizes.

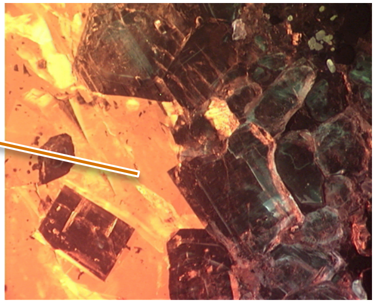
Methods/Approach

Mineral REE: Cathodoluminescence and LA-ICP-MS

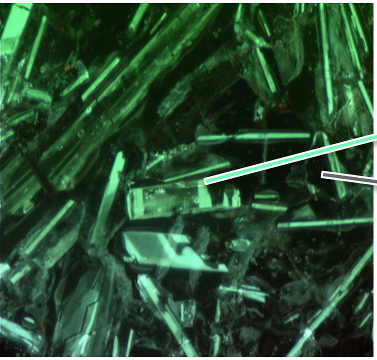
- We have developed techniques to identify REE enriched hydrothermal minerals using cathodoluminescence, and quantify REE by LA-ICP-MS.
- These relatively low-cost, short time frame analytical techniques promise to enhance evaluation of potential REE recovery sites and elucidate the geochemical behavior of REE.

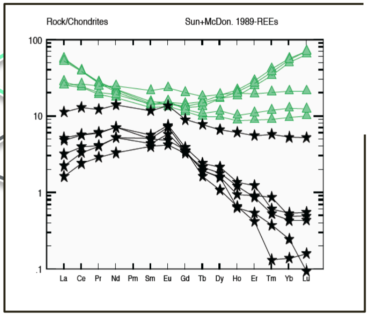
REE in calcite





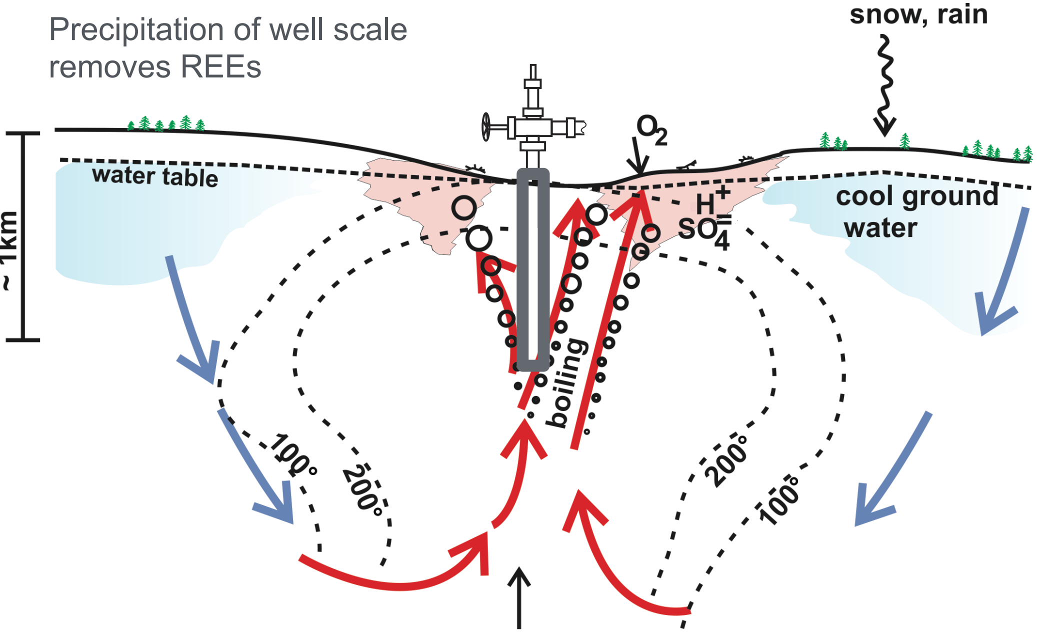
REE in anhydrite





Thermochemical modeling of REE leaching and precipitation

Completed a major addition of REE aqueous and mineral data to thermodynamic database SOLTHERM-xpt for use in CHIM-xpt and SOLVEQ-xpt



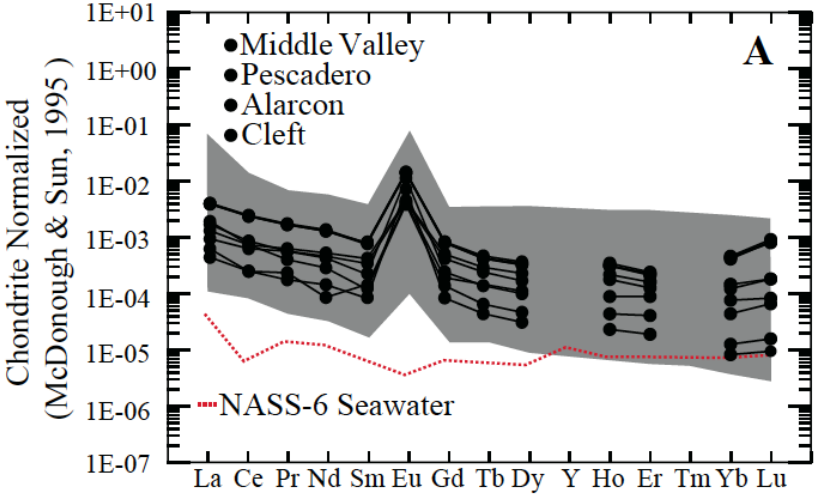
Precipitation of well scale removes REEs

Leaching of REE from host rock depends on REE complexing & solubilities of REE host minerals (apatite, epidote)

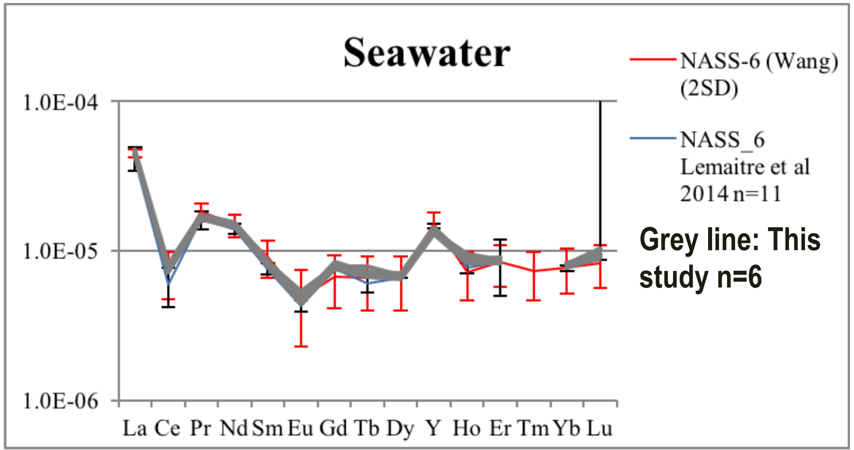
Technical Accomplishments and Progress

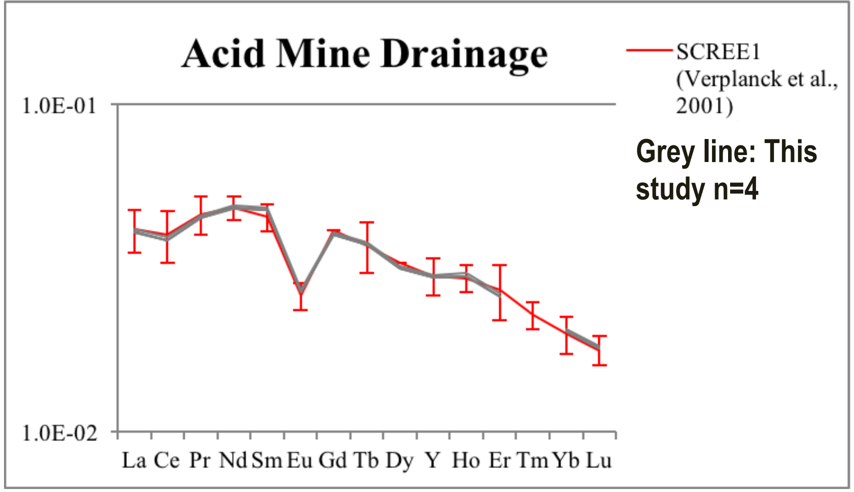
Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Milestone 1.1: Compilation of thermochemical data.	Completed	01/30/2015
Milestone 1.2: Summary report of compiled thermodynamic data.	Link uploaded to the DOE Geothermal Data Repository at http://gdr.openei.org/	09/15/2015
Milestone 2: Identification of well head fluid sampling sites; sampling agreements	Completed within limitations of access provided by geothermal operators	09/15/2015
Milestone 3.1: Well head fluid sampling and REE analysis	Analyzed 40 individual samples for REE, not including standards. Additional samples as available.	08/04/2017
Milestone 3.2: Data from year one will be compiled and uploaded to the GDR	Ten datasets have been uploaded to date, one pending as of Oct. 2017.	10/30/2017
Milestone 4.1: Decisions on location and timing of subsurface sampling will be made	Partnering with HS Orka to sample Reykjanes Geothermal field; waiting on window of sampling opportunity.	07/05/2016
Milestone 4.2: Analyses of down hole fluids will be completed	Well sampling scheduled for June 10-16, 2018.	Pending
Milestone 5: Run geochemical models that compare subsurface and well head geothermal fluids	Completed using down hole REE estimates, future models constrained by down hole sampling.	01/15/2017 Continuing improvements

Technical Accomplishments and Progress



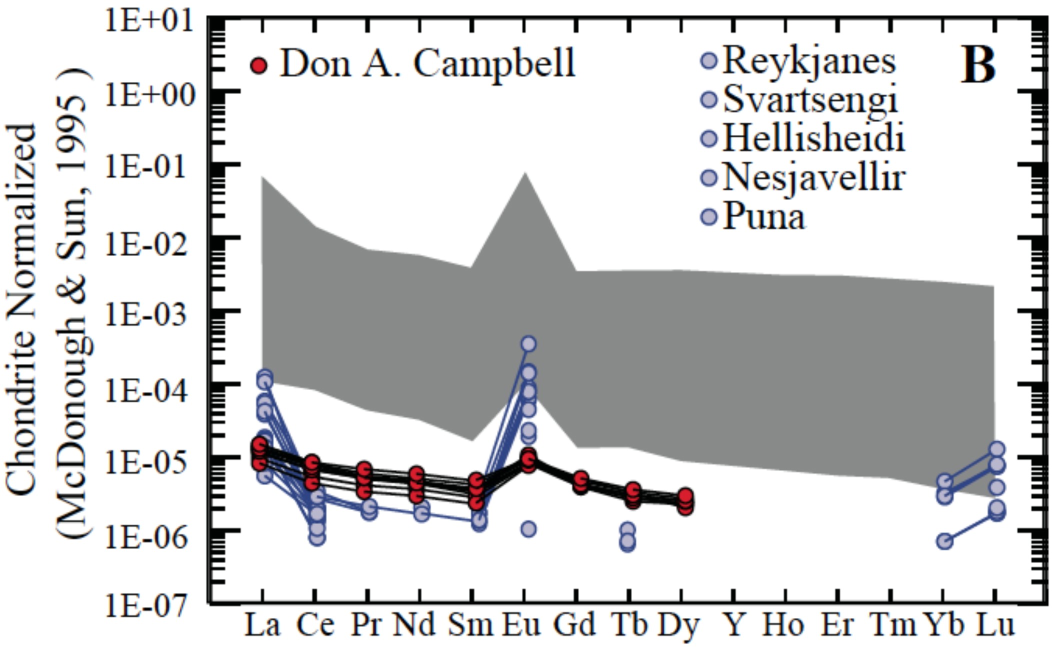
- Grey field is the range of REE in all submarine fluids from around the globe.
- Our submarine samples with a range of pH (~4 to 6) and Cl (+/- ~40% of seawater) fall in this field.
- Results show that the Cl and pH trend holds for these un-boiled fluids





- We verified our method on a range of sample and standards with challenging matrices: hydrothermal fluids, seawater, and acid mine drainage. Results are uploaded to the GDR.

Technical Accomplishments and Progress



1. High temp. (240° to >310° C) geothermal fluids (blue) with a range of pH (4 to ~8) and Cl <100 to >18,000 ppm) have remarkably similar REE.
2. Low temperature (~130° C) fluids from Nevada have higher concentrations for many REE
3. Boiling appears to be a major control and well head fluids are depleted in REE relative to formation fluids.
4. REE in geothermal fluids are limited by solubility constraints, not source rock availability.

Thermodynamic database: aqueous species (240+)

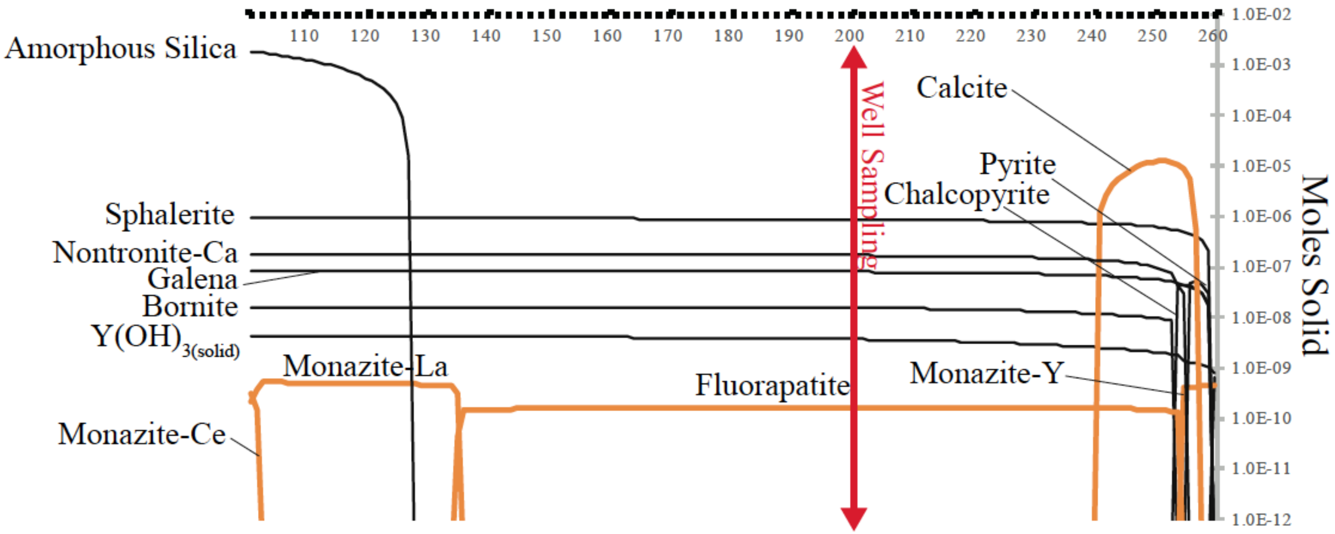
- **Trivalent free ions** that we selected to be thermodynamic components: Sc,Y,La,Ce,Pr,Nd,Pm,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu (Haas et al. 1995)
- **Divalent free ions**: La,Ce,Pr,Nd,Pm,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb (Haas et al. 1995)
- **Tetravalent free ions**: Ce,Pr,Nd,Pm,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu (Haas et al. 1995)
- **Oxy-hydroxides** of the trivalent ions: XOH+2, XO+, HXO2(aq), XO2- (Haas et al. 1995)
- **Carbonates**: XCO3+, XHCO3+2 (Haas et al. 1995)
- **Phosphates**: XH2PO4+2 (Haas et al. 1995)
- **Sulfates**: XSO4+, X(SO4)2- for Nd,Sm,Er (Migdisov 2008). Interpolated from these data, La,Ce,Pr,Eu,Gd,Tb,Dy,Ho,Tm,Yb,Lu
- **Halides**: XCl+2, XCl2+, XF+2, XF2+ of La,Ce,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu (Migdisov et al. 2009)
- **Complexes of divalent Eu**: EuCO3(aq),Eu(HCO3)+,EuCl+,EuF+,EuOH+ (Liu 2017)
- **Acetates**: X(Ac)+2 of La,Ce,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu (Ding2002)
- **Non-REE phosphates**: PO4-3,H2PO4-,H3PO4,CaPO4-,CaHPO4,CaH2PO4+,NaHPO4-,KHPO4-,FeHPO4,MgPO4-,MgHPO4,MgH2PO4+,MnHPO4 (Kharaka et al. 1988)

Thermodynamic database: minerals (70+)

- **Elements and sesquioxide** X2O3 forms except Pm (RH95, RHF78)
- **Hydroxides** X(OH)3 of Y,La,Pr,Nd,Eu,Gd,Tb,Ho (Diakonov et al. 1998a,b)
- **Florencite** XAl3(PO4)2(OH)6: La,Ce,Pr,Nd,Sm,Eu,Gd (Gaboreau & Vieillard 2004)
- **XPO4 monazite**: La,Ce,Pr,Nd,Sm,Eu,Gd, and **xenotime**: Tb,Dy,Er,Yb,Lu,Y (Migdisov et al. 2016)
- **Apatite-Ce-F** Ca4Ce(SiO4)(PO4)2F, **apatite-Y-F** Ca4Y(SiO4)(PO4)2F, and **monazite-Y** (Spear & Pyle 2010)
- **Carbonates** bastnaesite-Ce Ce0.5La0.25Nd0.2Pr0.05CO3F, and parisite-Ce CaCe.95La.6Nd.35Pr.1(CO3)3F2 (Gysi 2015)
- **Epidote group dissakisite-La** CaLaMgAl2(SiO4)3OH (Janots et al. 2007)
- **Epidote group Allanite** CaCeFeAl2(SiO4)3OH, and apatite-Ce Ca4Ce(SiO4)(PO4)2OH (Spear 2010)
- **Non-REE apatite-OH, apatite-F, apatite-Cl** (Zhu & Sverjensky 1991)

Database testing has resulted in refinements (as recently as August 2017) including disabling minerals with incorrect properties and finding better data for several species and minerals determined to be erroneous.

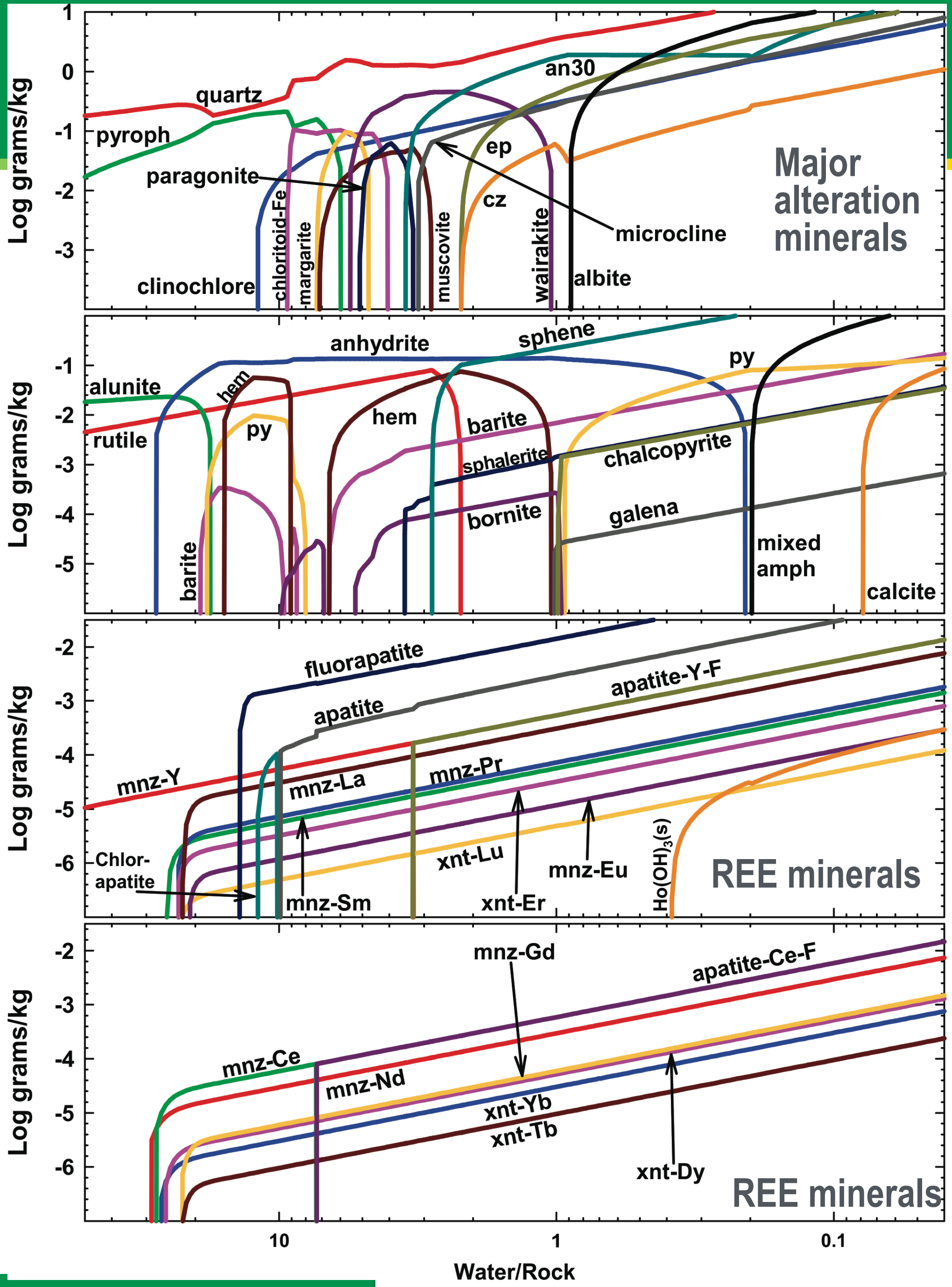
Technical Accomplishments and Progress



Example of a boiling calculation for well SV-7. Orange lines indicate potential REE controlling minerals.

- Requires estimation of downhole REE.
- Need measured downhole REE to verify models

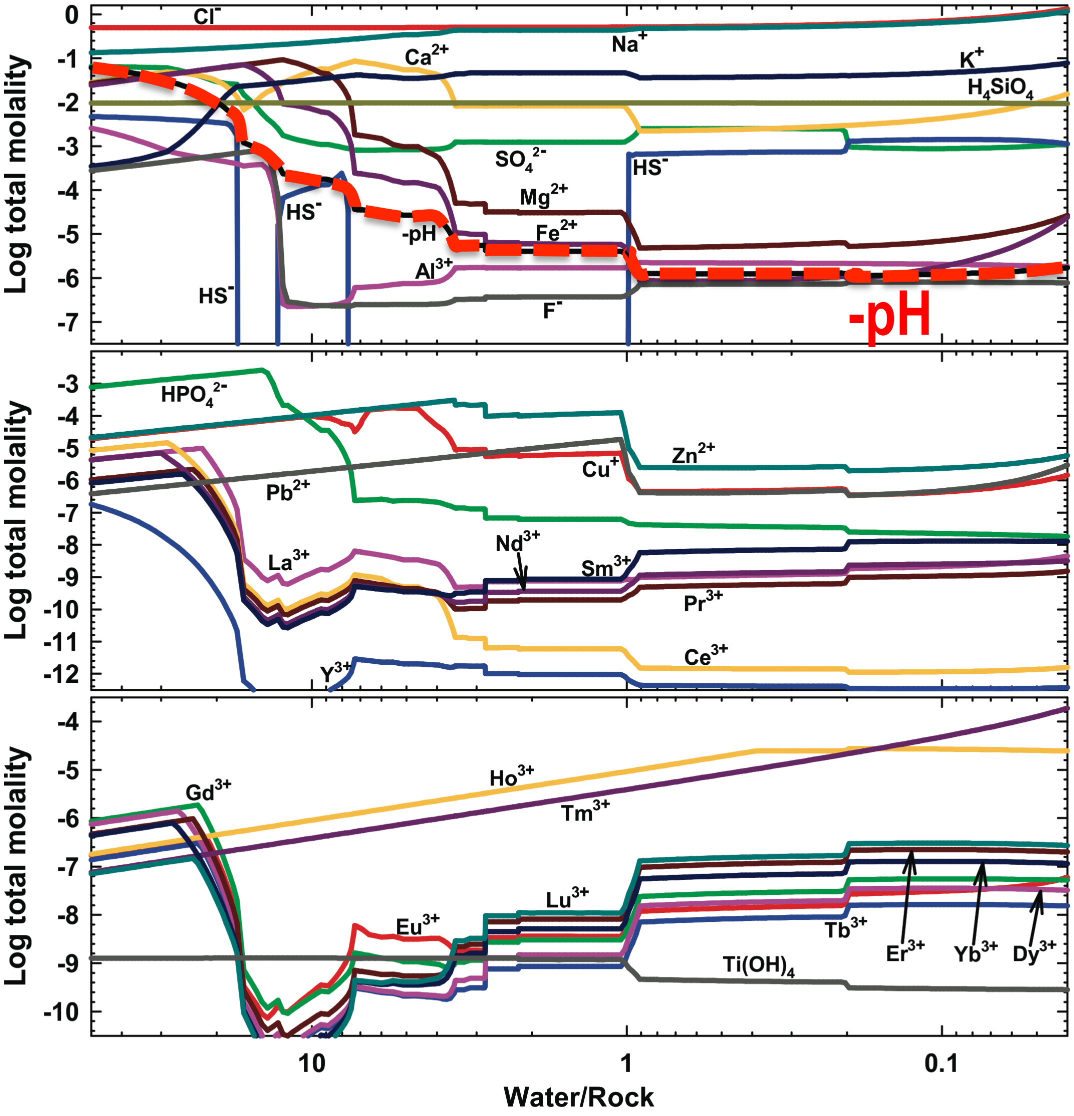
- Boiling models suggest REE are removed from fluids and incorporated into well scale by:
  1. Partitioning into major phases (e.g. calcite, fluorapatite)
  2. Formation of trace quantities of REE bearing minerals (e.g. monazite)
- Next step: verify boiling hypothesis using modeling and downhole samples from the lowest pH and highest Cl fluids: Reykjanes.
- Access limitations preclude sampling U.S. systems, but results will directly benefit U.S. geothermal operators.



CHIM reaction of andesite with acidic magmatic fluid + ground water at 300°produces:

- Silicate alteration:acid neutralization series: quartz through feldspars
- Sulfates, oxides, sulfides and carbonate

- REE phosphates: apatite, monazite, xenotime
- Epidote-allanite series is missing, owing to insufficient thermodynamic data. Dissakasite (epidote-like) does not precipitate.

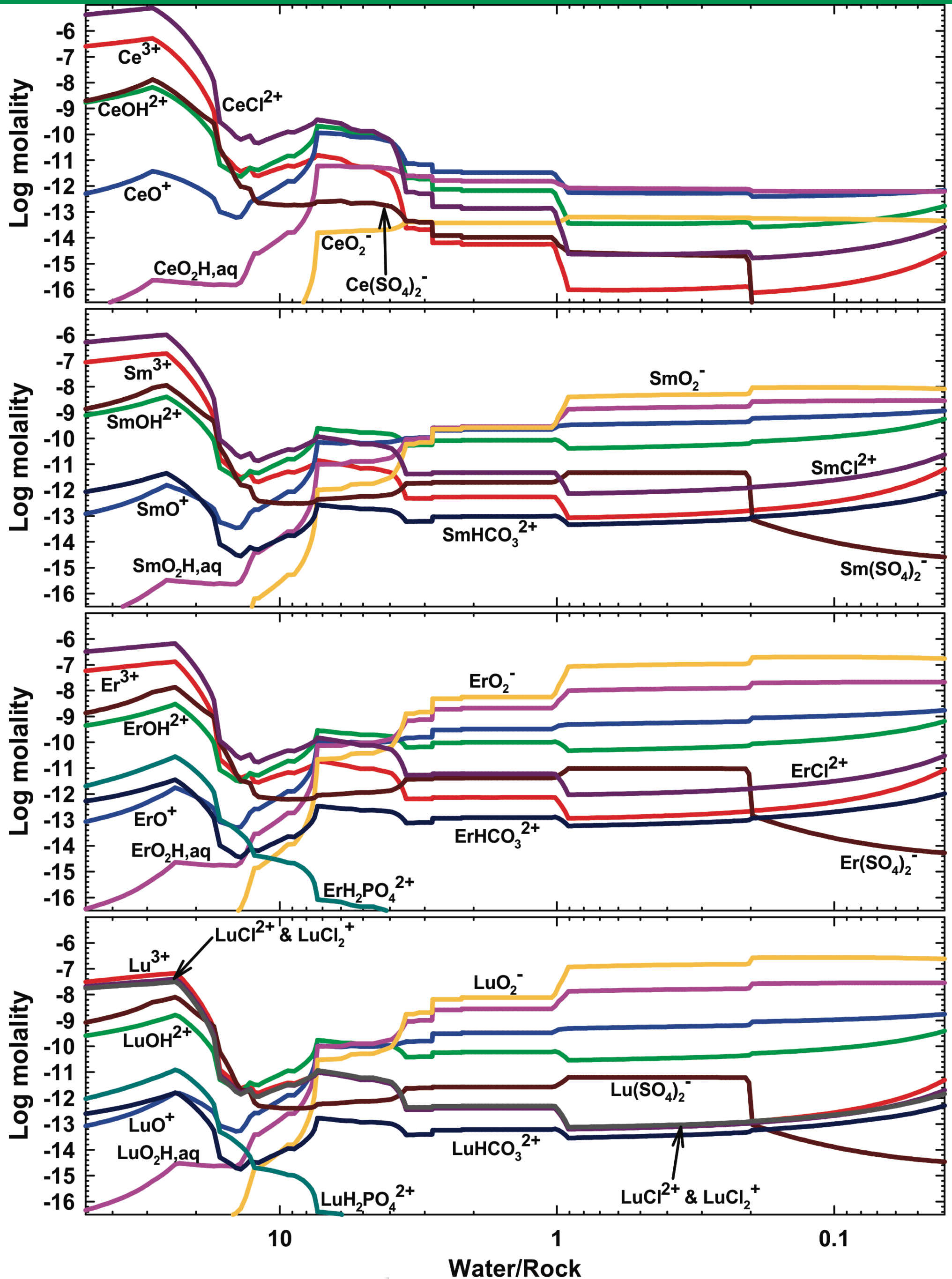


CHIM reaction of andesite with acidic magmatic fluid + ground water at 300°:

Total molalities & pH

- Major component species
- Minor metals
- REEs

- REE concentrations are limited by phosphate minerals as acid is neutralized, except for Ho and Tm, for which we had no mineral phosphate thermodynamic data.



CHIM reaction of andesite with acidic magmatic fluid + ground water at 300°:

Molalities of REE complexes of Ce, Sm, Er, Lu (as examples of light and heavy REEs)

- Chlorides & bare ions dominate at low pH, joined by sulfates at moderately acidic pH
- Oxyhydroxide ligands dominate at neutral pH
- Carbonate and phosphate ligands are minor players in this fluid composition

Research Collaboration and Technology Transfer

- Summarize any industry or academic engagement that is taking place under this project.
  - One Ph.D. Andrew Fowler produced with geothermal expertise
  - One MS student Carolyn Cantwell produced with geothermal expertise
  - Seafloor hydrothermal vents sampled by MBARI provided at no cost to DOE
  - Established working relationship with HS Orka and IDDP.
- Describe opportunities or efforts currently underway to transition technology to the private sector.
  - Three peer reviewed publications to date.
  - Three publications in preparation or submitted.
  - All data submitted to the DOE Geothermal Data Repository
  - Geochemical modeling software and data base containing REE thermodynamic data available through the University of Oregon web site.

Mandatory- may utilize multiple slides

Future Directions

- Down hole fluid sampling scheduled for July 2017 was cancelled at the last minute due to unavailability of wire line service support.
- High enthalpy fluids will be collected down hole below the boiling horizon in wells from which we have previously analyzed fluids collected at the well head and analyzed REE concentrations in primary igneous and secondary alteration minerals and scale samples.
- Samples will be collected in trace element clean, gas-tight, internally filtered sampler allowing complete analyses and reconstruction of the the fluid properties including T, P, pH, major & trace element, REE, and gas composition.
- Modeling of down hole and well head fluids will be used to evaluate the adequacy of REE thermodynamic data and suggest approaches to advance our knowledge.

Milestone or Go/No-Go	Status & Expected Completion Date
Downhole Sampling	Scheduled for June 10-16, 2018 during scheduled well and turbine maintenance. Wire line support provided by HS Orka leveraging our DOE funding.

Mandatory Summary Slide

- We developed techniques to measure sub-ppt concentrations of many REE in geothermal brines
- We developed predictive models to quantify processes that control REE concentrations in geothermal fluids.
- We have shown that REE are present at much higher concentrations in subsurface geothermal reservoir fluids compared to well head fluids that have undergone phase separation.
- We have generated numerous publications and publically available datasets
- Our next step is to sample un-boiled down hole fluids down hole to provide a quantitative assessment of REE transport and mineral partitioning.