Maximizing REE Recovery in Geothermal Systems

Project Officer: Arlene Anderson

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Track 1: Systems Analysis & Low Temp

Project Objective - Knowledge gaps and problems being address by this project:

- Quantify the Rare Earth Element (REE) content in hydrothermal fluids from "end-member" geothermal fields selected to maximize understanding of the different factors that contribute to REE solubility.

- Evaluate the effect boiling and mineral precipitation on the partitioning of REE through down hole fluid sampling and high spatial resolution REE analyses of hydrothermal minerals.

- Incorporate the best available thermodynamic data into geochemical modeling programs in order to evaluate the ability to accurately model the fluids and solids we analyze, and identify data gaps for improvements of geochemical modeling codes and data bases.

- Quantify the potential economic benefits of co-recovery of REE in the systems evaluated.

Relevance/Impact of Research

Innovative Highlights:

- Ion exchange technology and high resolution ICP-MS to accurately measure REE contents in geothermal fluids.

- Laser Ablation ICP-MS analysis of REE individual hydrothermal minerals

- Direct investigation of REE partitioning between fluids and minerals, and due to downhole flashing; essential knowledge for determining the REE flux in geothermal systems.

- Incorporation of REE thermodynamic data into geochemical modeling programs.

Relevance to GTO goals:

- The existing data on REE concentrations in geothermal fluids is presently inadequate and precludes realistic economic evaluation of REE recovery.

- Isolate the critical variables that contribute to REE solubility in different types of geothermal systems, combined with improved modeling capabilities, to allow extrapolation of our results to other geothermal systems.

- Provide the data necessary to quantitatively evaluate the economic trade offs of mineral recovery vs power in plant design and operation.

Ion-exchange technology

- Data on the REE content of geothermal fluids is very limited,

- Challenging to analyze due to low concentrations of REE with high concentrations of interfering elements typical of geothermal fluids.

- We have successfully analyzed high-temperature, saline fluids from Reykjanes using ion exchange separation and high-resolution inductively coupled plasma mass spectrometer (ICP MS) which provides a direct comparison to 'unflashed' seafloor hydrothermal fluids.
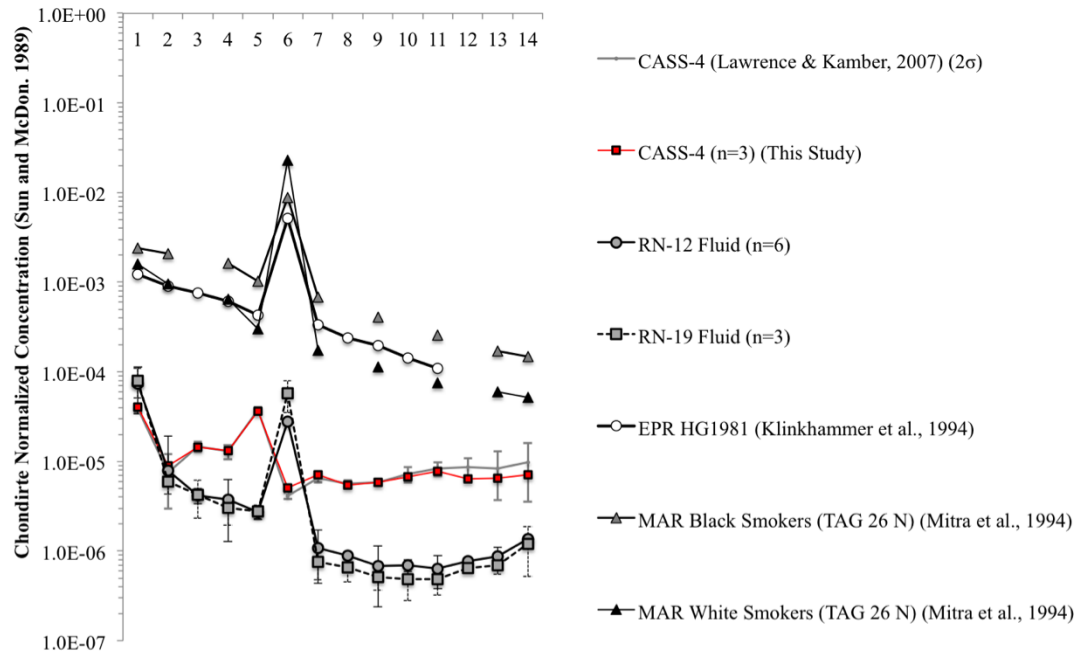
Collect down hole and well head samples

- REE in wells generally increase as a function of Cl, while surface springs that have undergone boiling, oxidation, or mixing fall away from this trend.

- The REE content of well fluids is likely modified by flashing. A primary objective is to quatify this process through downhole fluid sampling and LA ICP-MS analyses of hydrothermal minerals in upcoming quarters.
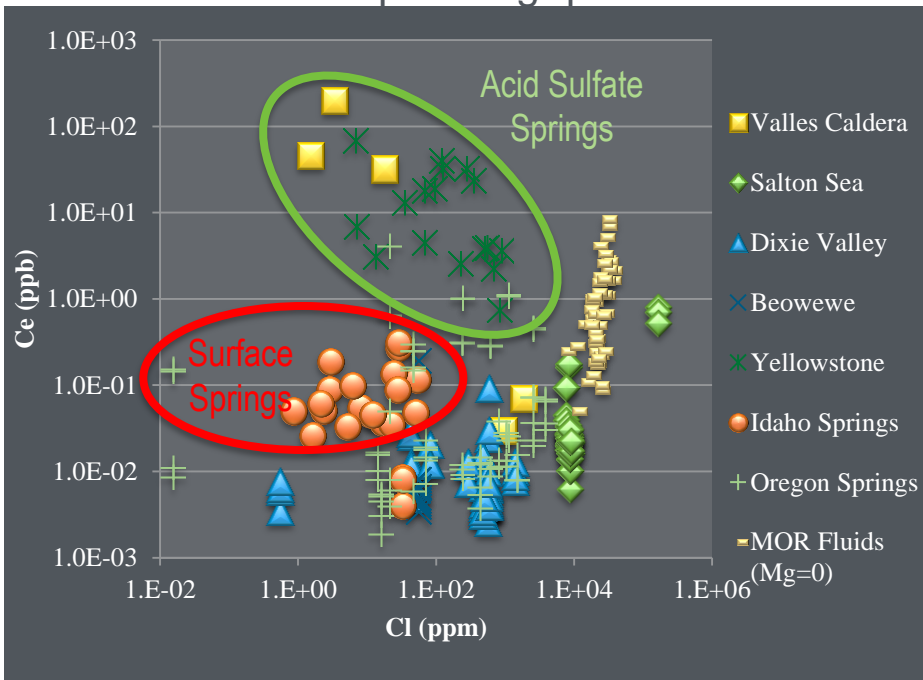

Cerium in both springs and wells
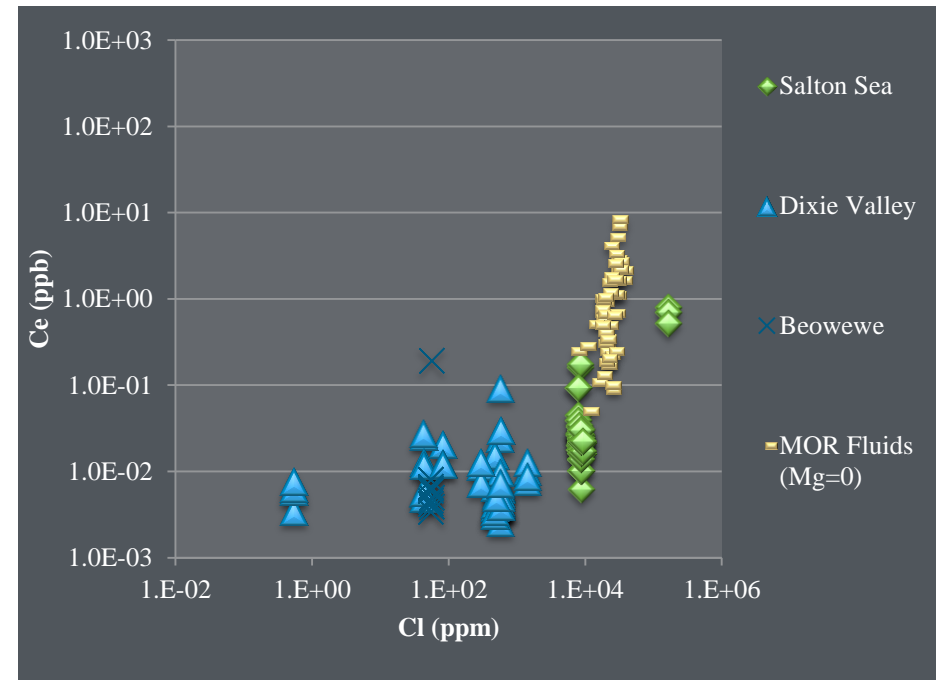
Cerium in wells only

Evaluate the REE content of hydrothermal minerals

- Refine our ability to conduct high-spatial resolution REE analysis on hydrothermal minerals using 193nm excimer laser ablation (LA) coupled to a quadrupole ICP MS.

- Our on-going investigation of the REE content of hydrothermal minerals using LA-ICM MS recovered from wells sampled for geothermal fluids will help guide the selection of sampling sites.

Epidote Well RN-12

Fluids Well RN-12 and RN-19
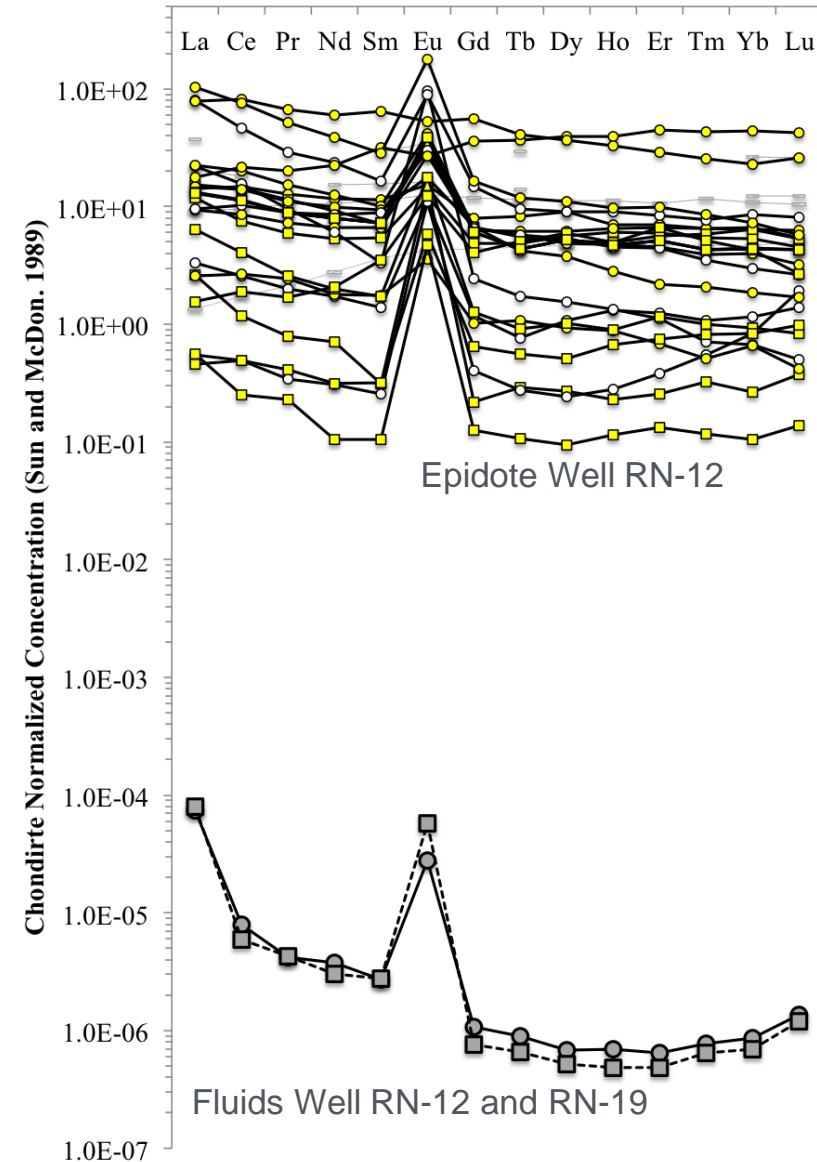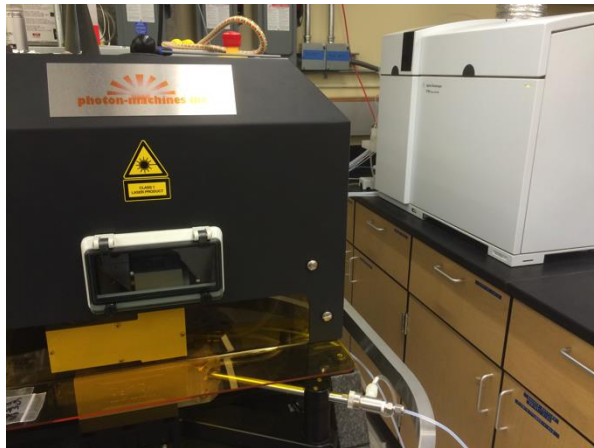
Thermochemical modeling goal is to understand REE chemical behavior in hydrothermal systems

- Compute simultaneous aqueous-mineral-gas equilibria applicable to geothermal processes:
    - Boiling as a cause of REE-bearing scale precipitation
    - Fluid-fluid mixing and effect on REE mineral precipitation
    - Leaching of REE's from host rocks: pH and redox effects
- **Compilation** of REE thermodynamic data
    - H,S, V and Cp(T) thermochemical data for aqueous REE species and minerals
- **Model reconstructed geothermal fluids** including REE concentrations to work out controls on REE concentration in primary fluids and causes of REE mineral precipitation in specific settings.
- **Evaluate** possible REE recovery systems as input to power plant design and operation.
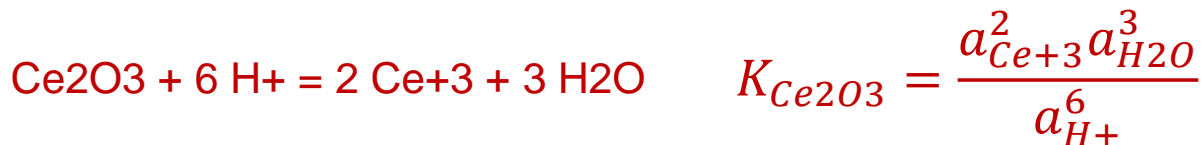
(Thermochemical modeling is by Mark Reed and James Palandri, University of Oregon.)

REE thermodynamic data: log K's for basic equilibria at P,T

- In the SOLTHERM database, minerals and derived aqueous species (complexes, etc.) are expressed as a linear combination of component species.

- For REE and related elements, aqueous component species:

La+3	Nd+3	Eu+3	Dy+3	Tm+3		Sc+3
Ce+3	Pm+3	Gd+3	Ho+3	Yb+3		Y+3
Pr+3	Sm+3	Tb+3	Er+3	Lu+3		

- Equilibrium constants K are expressed in terms of these and other component species; e.g. for CeCl2+ (derived aqueous species) and Ce2O3 (mineral):

CeCl2+ = Ce+3 + 2 Cl-

$$K_{CeCl2+} = a_{Ce+3}\, a_{Cl-}^2$$

Ce2O3 + 6 H+ = 2 Ce+3 + 3 H2O

$$K_{Ce2O3} = \frac{a_{Ce+3}^2 a_{H2O}^3}{a_{H+}^6}$$

K's are computed with SUPCRT using equation of state (EOS) parameters for aqueous species, and, for minerals, also using $\triangle$G, S, Cp and V. Some K's are tabulated directly from literature sources, with compatibility adjustments as needed.

REE thermodynamic data: Aqueous species

- REE EOS data already in the SUPCRT database, estimated from compiled experimental data and correlation algorithms by Haas et al. 1995 include:
  - The +3 component species listed above
  - REE ions of +2 and +4 charge, as appropriate
  - Complexes with Cl- F-, oxyhydroxide, phosphate, acetate:

MCO3+	MO+	MCl+2	MCl4-	MF+2	MF4-	M(Ac)+2
MHCO3+2	MO2H,aq	MCl2+	MH2PO4+2	MF2+	MSO4+	M(Ac)2+
MOH+2	MO2-	MCl3,aq	MNO3+2	MF3,aq		M(Ac)3,aq

  - Additional Eu+2 complexes with the above ligands

- Log K's are also present for organic complexes of higher molecular weight than acetate, but log K's were not computed for those.

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REE thermodynamic data – Aqueous species

Since the publication of REE data by Hass et al. (1995), two additional publications provide additional or revised data:

- Data for Nd, Sm, and Er mono and disulfate complexes compiled as log K's (Migdisov et al. 2008), using their own experimental data and an improved activity model. These data are in reasonable agreement with Haas et al. 1995 for the monosulfate complexes. For disulfate complexes at low T there is also agreement with the previous work, but at T > 150 C, greater stability is predicted, in agreement with their data.

- Data for all REE (except Pm), as halide complexes $MCl+2$, $MCl2+$, and $MF+2$, compiled as SUPCRT EOS parameters (Migdisov et al. 2009). These data were formatted for, and put in the SUPCRT database and log K's were computed. The most significant differences from the earlier compilation of Haas et al. 1995 are that at elevated T, light REE fluoride and light REE chloride complexes are more stable than heavy REE counterparts.

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REE thermodynamic data – Minerals

REE ΔG, S, V, and Cp, data added to the SUPCRT database

- Elements, and sesquioxides (M2O3), for the following:

La	Nd	Gd	Ho	Yb		Sc
Ce	Sm	Tb	Er	Lu		Y
Pr	Eu	Dy	Tm			

  and cerianite CeO2 and EuO from Robie, Hemingway, and Fisher, 1978.

  Cp data re-regressed to conform to Cp equation of Holland and Powell.

  (Note: only Ce and cerianite are carried over to Robie and Hemingway, 1995.)

- Monazite-La (LaPO4) and dissakisite-La (CaLaMgAl2(SiO4)3OH; epidote analog) from Janots et al. 2007.

- Y(OH)3, Pr(OH)3, Eu(OH)3, Gd(OH)3, Tb(OH)3, and Ho(OH)3 from Diakonov et al., 1998a. Molar volume from Milligan et al. (1979).

- La(OH)3(s), and Nd(OH)3(s) from Diakonov et al., 1998b.

- We are currently reducing the methodology of Gaboreau and Vieillard, 2004: "Prediction of Gibbs free energies of formation of minerals of the alunite supergroup," for predicting properties of REE minerals from those of their oxides.

Accomplishments, Results and Progress

| Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Milestone 1.1 due Q1: Compilation of thermochemical data for REE aqueous species and minerals.	Achieved as stated	February 2015
Milestone 1.2 due Q2: Summary report of compiled thermodynamic data.	Current with proposed deadline. Undergoing model testing and data review.	In Progress
Milestone 2 due Q2:Identification of well head fluid sampling sites	In progress and currently ahead of schedule. Previous REE data compiled. Active USA geothermal sites identified.	In Progress
Milestone 3.2 due Q5: Well head fluid sampling and REE analysis	The mineral REE analytical portion of this milestone is underway with LA-ICP-MS testing	In Progress (design phase)

Extra: A data compilation not previously listed in the SOPO will be provided to the online data repository and has already been provided to support other teams.

Technical Challenges: No significant technical challenges have been encountered.

Compiled existing fluid REE data to inform sampling site selection

- We identified 288 thermal fluid samples with REE data from the United States and 161 fluid REE samples from MOR systems from 46 submarine vent locations.

- We identified locations previously sampled for REE (White) and operating geothermal systems with no REE data (red).
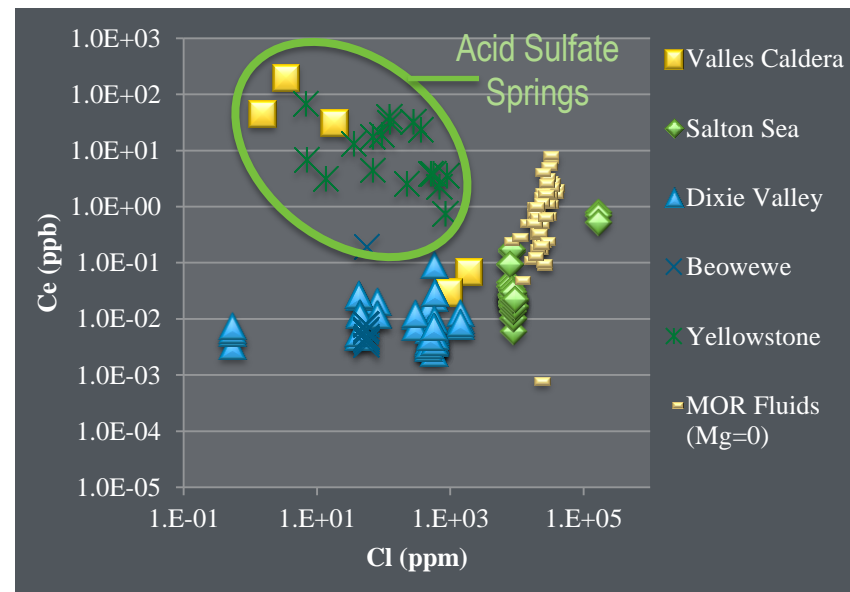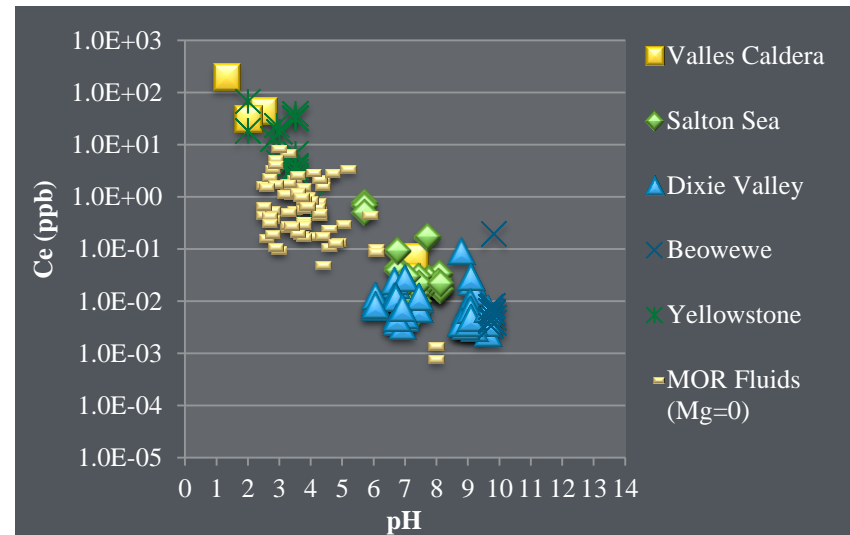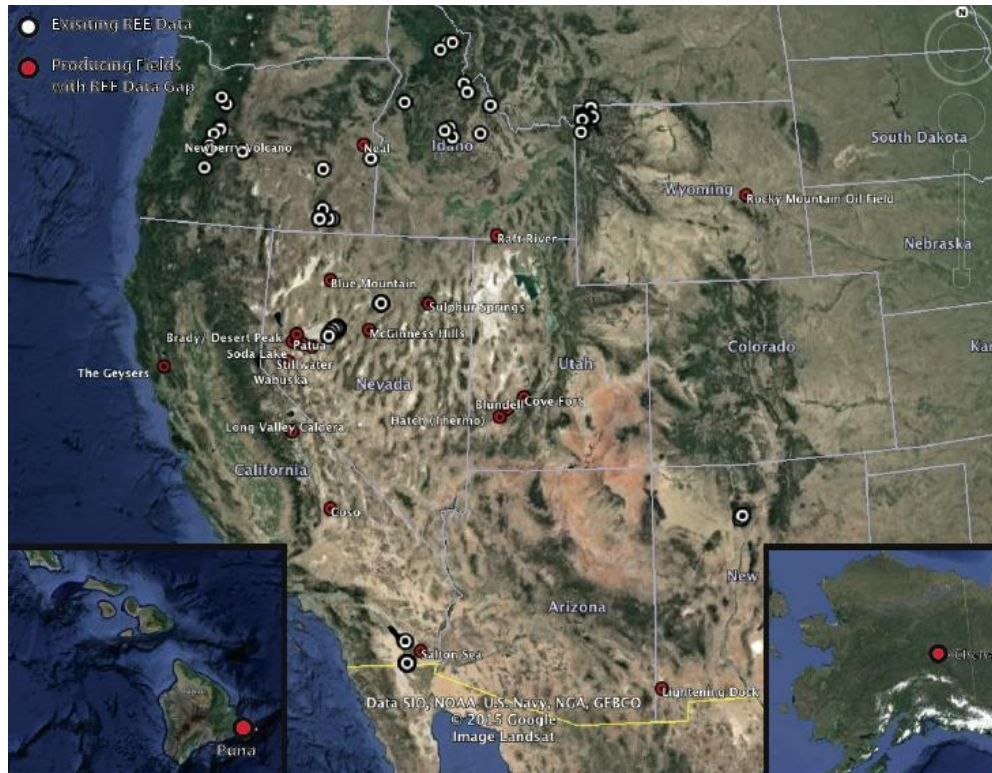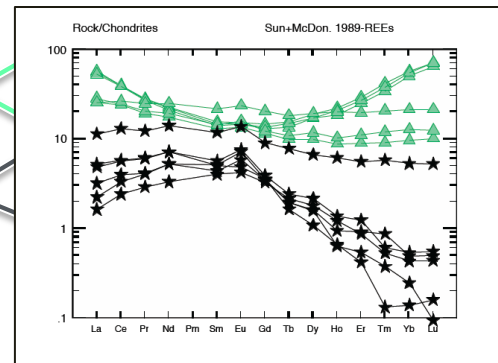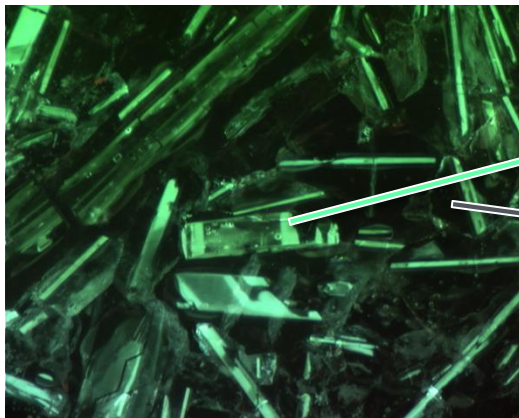
Mineral REE: Cathodoluminescence and LA-ICP-MS

- We have developed techniques to identify REE enriched hydrothermal minerals using cathodoluminescence, confirmed by LA-ICP-MS.

- These relatively low-cost, short time frame analytical techniques promise to enhance evaluation of potential REE recovery sites.
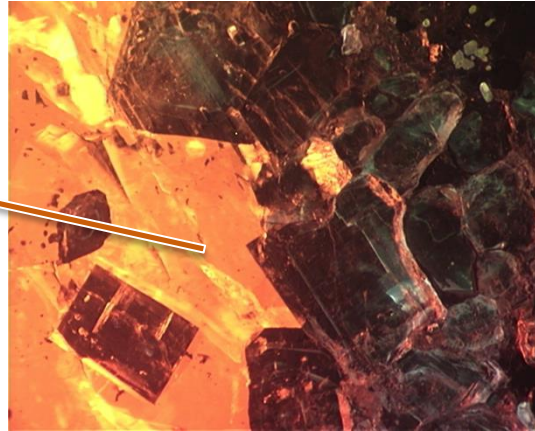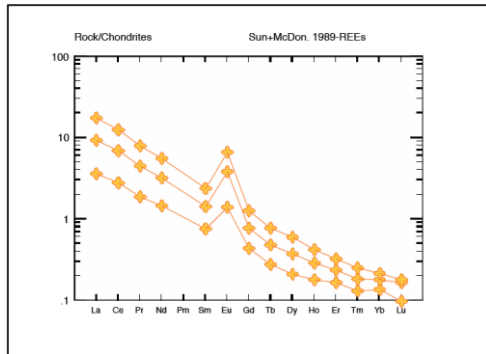
REE in calcite

REE in anhydrite

Future Directions

Milestone or Go/No-Go	Status & Expected Completion Date
Milestone 1.2 due Q2: Summary report of compiled thermodynamic data.	In progress and current with proposed deadline. Undergoing model testing and data review.
Milestone 2 due Q2: Identification of well head fluid sampling sites	In progress and currently ahead of schedule. Previous REE data compiled. Active USA geothermal sites identified. Anticipated completion June 2015.
Milestone 3.1 due Q4: Well head fluid sampling and REE analysis	Pending completion of sampling agreements. Anticipated completion March 2016.
Milestone 3.2 due Q5: Analyses of well head samples for REE content.	Pending completion of sampling agreements. Anticipated completion June 2016.

Extra: Fluid REE samples from Alarcon Rise, a seafloor hydrothermal system are currently being collected and will be provided to the project at no extra cost. The pressure of overlying seawater prevents the fluids from phase separating and losing REE to mineral phases. This data is essential to provide high-temperature constraints to our models

Obstacles: The ideal sampling site list will be modified based on site operations. Final sample sites will be determined by availability (i.e. Wells planned for maintenance or sampling)

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Summary of Key Points

- Our project is taking an innovative approach and utilizing state-of-the-art facilities to provide high-quality data to DOE-GTO.

- These data are necessary for quantifying economic benefits of REE recovery

- Our process-based approach to sampling end-member systems couple with improvements of thermodynamic modeling will facilitate extrapolation of our analytical results to other systems.

- Currently on schedule for all tasks, and ahead of schedule for several tasks, with value added samples of opportunity included at no additional cost to the project.