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Assessing REE concentrations in geothermal and O&G Produced waters: A potential domestic source of strategic mineral commodities

Scott Quillinan
School of Energy Resources
Carbon management Institute

Track 1: Mineral Recovery

Project Officer: Holly Thomas

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Project team and Industry Collaborators

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University of Wyoming

Scott Quillinan

J. Fred McLaughlin

Jonathon Brant

Idaho National Labs

Travis McLing

Ghanashyam Neupane (Hari)

USGS

Mark Engle-Eastern Energy Resources Science Center

Timothy Bartos-WY/MT Water Science Center

UNIVERSITY OF WYOMING CEPWM

Carbon Management Institute
SCHOOL OF ENERGY RESOURCES
UNIVERSITY OF WYOMING

CAES Center for Advanced Energy Studies

INL Idaho National Laboratory

USGS science for a changing world

Industry Collaborators

GE

ExxonMobil

PACIFIC POWER
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BASIN ELECTRIC POWER COOPERATIVE
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AETHON

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Project goal and objectives

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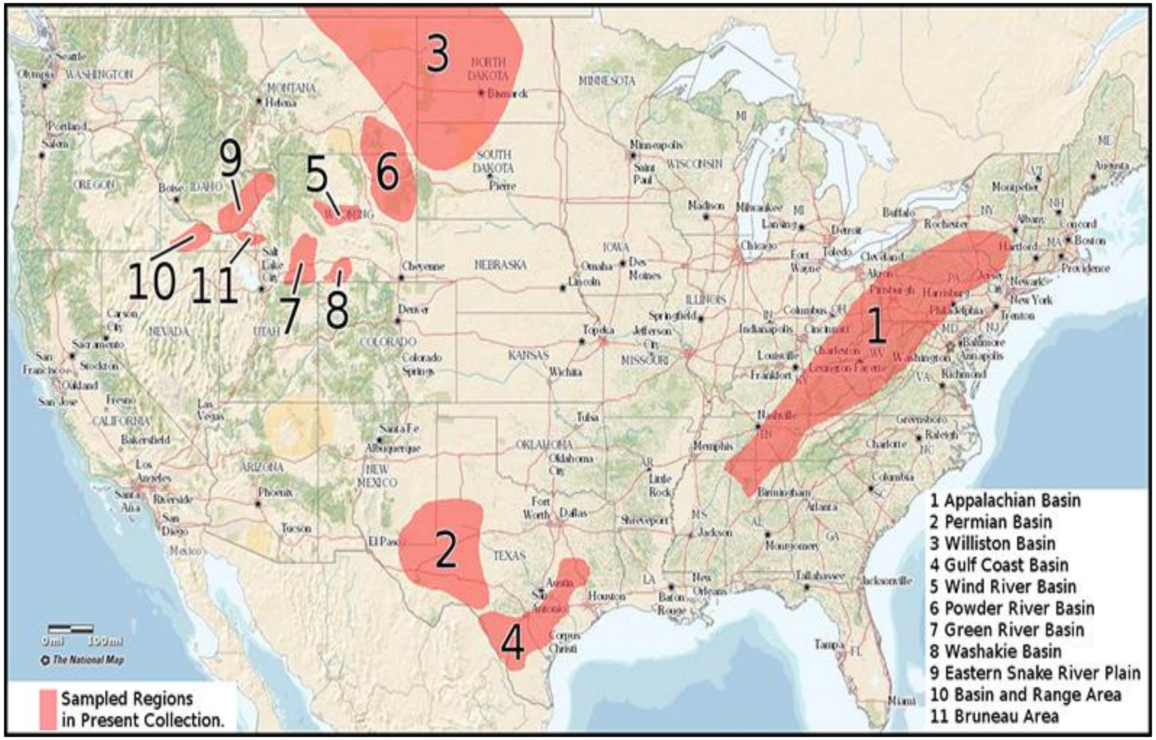
Assessing rare earth element concentrations in geothermal and oil and gas produced waters: A potential domestic source of strategic mineral commodities

Project Goal:

1) Contribute to a national database of rare earth element and high value materials in oil and gas produced waters and other geothermal waters
2) Refine methodologies for REE analysis in high saline fluids
3) Develop a statistical screening tool for geologic prospecting
4) Techno-economic assessment



Relevance to Industry Needs and GTO Objectives

- Create a first of its kind public database of REEs in produced waters
- Broaden the scope of groundwater science
  - Groundwater tracing
  - Help define complex geochemical processes
  - Identify reservoir mixing
  - Basin evolution
  - REE mobility and transport
  - Diagenesis
- Could fundamentally change the way oil and gas waste streams are managed

Elements of interest in the study

Element	Type	Applications	Element	Type	Applications
Ce[1]	REE	Oxidizer and catalyst	Mn[1]	Trace	Steel alloys and production
Co[1]	Trace	Batteries and alloys	Nd[1]	REE	Magnets and capacitors
Dy[1]	REE	Magnets and minor alloys additive	Ni[1]	Trace	Multi-purpose metal
Er	REE	Lasers and steel alloys	Pr[1]	REE	Radioactive decay heating
Eu[1]	REE	Lighting and NMR	Sc	REE	Catalyst and lighting
Ga[1]	Trace	Photovoltaics and semiconductors	Sm	REE	Magnets and neutron flux control
Gd	REE	Neutron flux control and many alloys	Tb[1]	REE	Magnets and lasers
Ho	REE	Magnets and lasers	Th	Trace	Fuel and lighting
In[1]	Trace	Photovoltaic film	Tm	REE	Lighting and lasers
La[1]	REE	Catalyst and glass additive	U	Trace	Fuel and ballast
Li[1]	Trace	Flux and batteries	Y[1]	REE	Lasers and steel alloys
Lu	REE	Medical tracer and glass additive	Yb	REE	Reducing agent and steel alloys

[1] DOE identified critical material

Project alignment with GTO objectives

- Overcoming technical obstacles (method development)
- Demand for subsurface data
- Accessing additive values
- Collaborating on subsurface energy challenges
- Supporting early stage R&D…strengthening the body of knowledge to accelerate development

Task 1 Collect matching/analogous rock and water samples *(UW, INL, USGS)*

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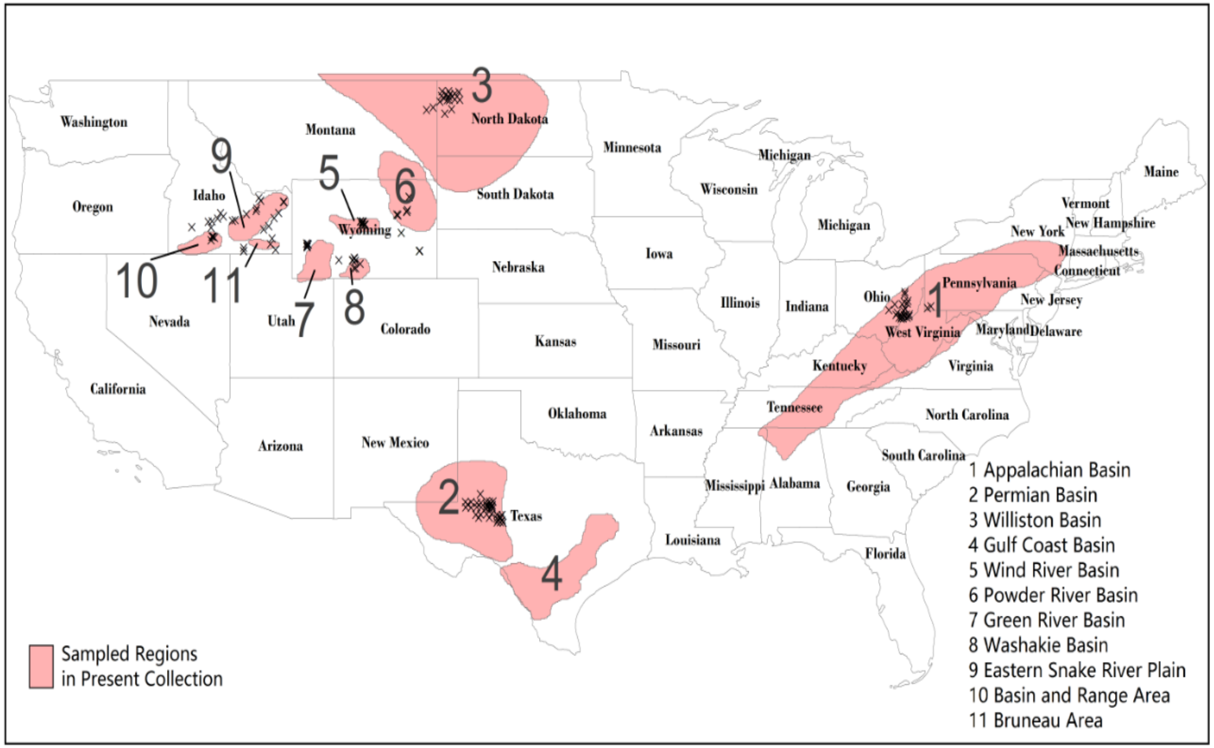
- **Goals**: Expand existing water and rock collections through industry collaborations
- **Action:** Collect matched pairs of water and rock samples from oil and gas wells and some hydrothermal springs
- **Product:** This Task will provide sample material for all subsequent tasks



Geologic Basin	No. of Samples
1) Appalachian	19
2) Permian	14
3) Williston	20
4) Gulf Coast	39
5) Wind River	16
6) Powder River	10
7) Green River	6
8) Washakie	8
9,10,11) Geothermal Waters	33
Industrial Waters	10
Total	**175**

T1.1 Sample and analysis plan

<u>In the Field</u>

- Samples are collected directly from the oil and gas separator
  - Wells are flowing at the time of sampling, obviating the need to remove several casing volumes
  - Four 500 ml LDPE, acid washed bottles
    - Filled to overspill to eliminate head space
  - Collect one field blank using nano pure water
  - Collect field parameters pH, EC, dissolved oxygen (ORP), temp
  - Iced for transport

<u>In the Lab</u>

- Frozen over night to halt microbial activity
- Filtered through 0.45 μm millipore cellulose acetate filters
- Acidified samples (pH of <2 with trace metal grade nitric acid)
  - 500 mL for REE in a clean 500ml bottle
  - 15 mL test tube ICP-OES
  - 15 mL Energy Labs (Cations)
- Non-acidified samples
  - 30 mL Wheaton vial stable isotope analysis (D, O, DIC)
  - 50 mL Isotech (D, O, Sr)
  - 50 mL Energy Labs (Anions)
  - 500 mL back-up sample

T1.2 Identify rock sample locations

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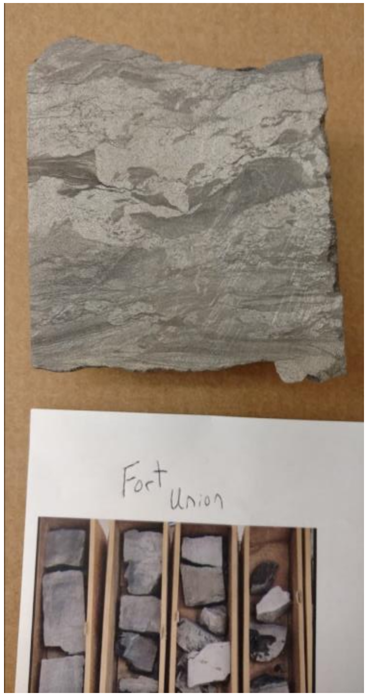
- 88 geologic reservoir samples were collected
- Represent 15 different reservoirs
- All but the three newest of the formations are represented (waters collected this year)
- As additional water samples are analyzed we will continue to add rock samples



Paleocene Fort Union Core

Geologic Formation	No. of Water Samples	No. of Rock Samples
Almond	4	5
Cody	2	0
Fort Union	11	10
Frontier	4	11
Frontier/Baxter	2	8
Lance	3	0
Lewis-Almond	4	7
Maddison	3	13
Mesa-Verde	1	0
Mowry	1	4
Muddy	2	6
Niobrara	2	13
Parkman	2	4
Shannon	1	4
Turner	2	5

Milestone 1.3

Task 2- Characterize oil and gas produced waters and some geothermal waters *(UW and INL)*

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- **Goals**: Quantify water samples through analytical techniques
- **Action:** Laboratory analysis and preliminary geologic interpretation
- **Product:** Aqueous parameters needed for geostatistical analysis and technological screening Task 5 & 6

T2.1 Analysis of geochemistry for new OGTW samples
- Minor, Major and Trace elements
- Stable isotope analysis

T2.2 REEs characterization of fluid samples following selective pre-concentration
- Using INL methodologies quantify REEs in all transferred waters samples

T2.3 Research or collect flow rate and temperature data from samples
- Flow rates and temperature data will be researched from regulatory databases or measured during sample collection

Subtask 2.4 Geochemical Interpretation
- Estimate water/rock reactions
- Fluid origin and evolution
- REE Occurrence and distribution
- REE transport

REE Method Development

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Barriers to REE quantification

High Salinity (esp. barium)

Challenges:

- Fluctuating baseline
- Direct carrier-gas mass interferences

Improvements:

- Using methods Strachan et al. (1989)…And large sample size (1L)
- Extraction through resin-chromatography
- Analyze through standard ICP-MS

Dissolved hydrocarbon

Challenges:

- Resin Clogging
- Damage the quality of the extraction

Improvements:

- Running under pressure
- Two passes through resin make a good quality extract
- Speed and quality improved

Small Sample Volume

Challenges:

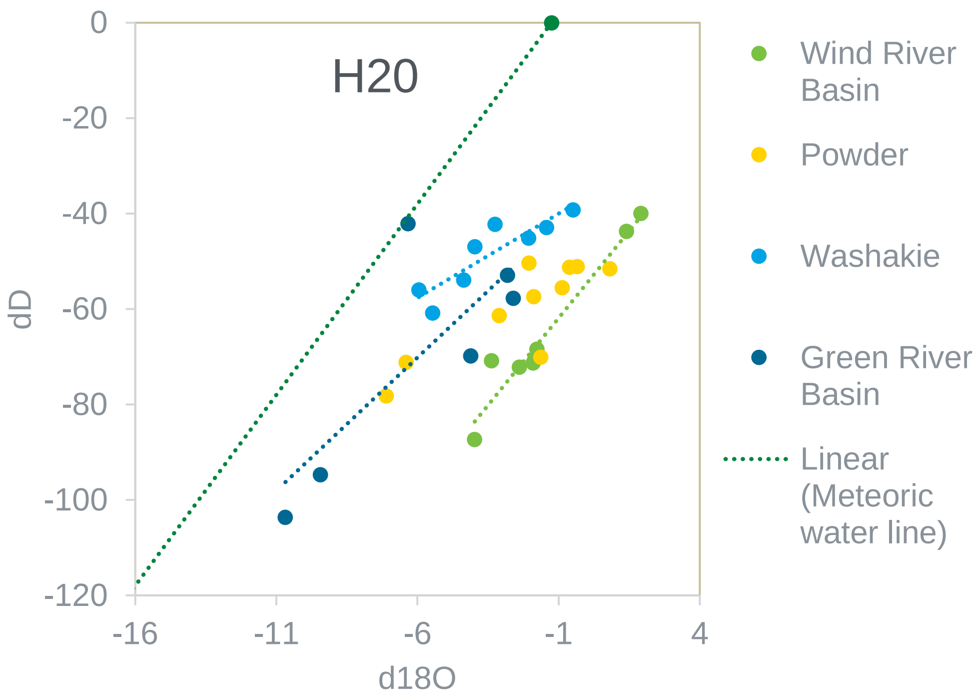
- Slightest contamination could skew results by a significant percentage
- Difficult to preconcentrate to guarantee detection by ICP-MS

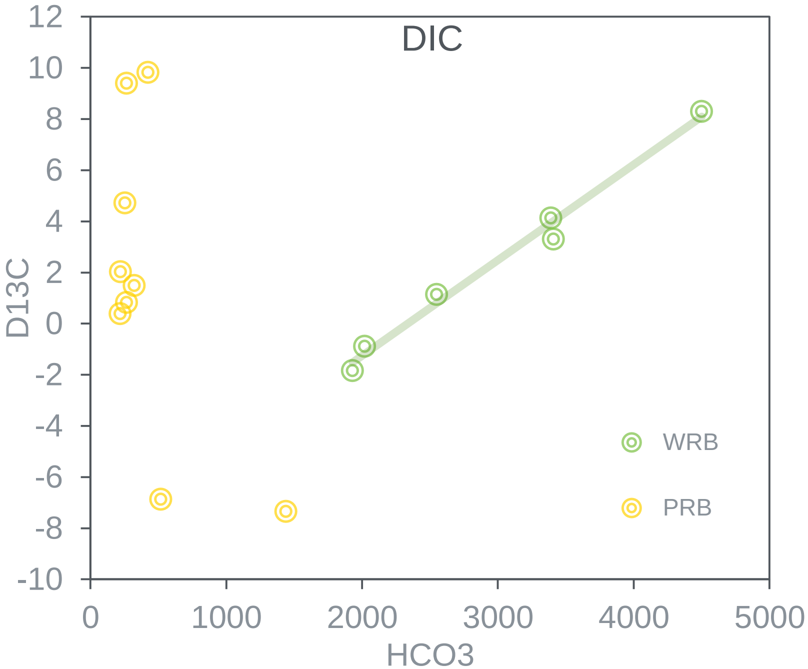
Improvements:

- Secondary enclosure
- Blank statistics

Stable Isotope Data

Isotopes: δD, δO¹⁸, $\delta^{13}C_{DIC}$





H_2O

- δO¹⁸ isotopes heavy enriched
- Indicate water/rock interaction

<u>¹³C of Dissolved inorganic carbon</u>

WRB indicate biogenic gas

Enriched signature but missing CO_2

Selected REE patterns normalized to North Pacific Deep Water (NPDW)

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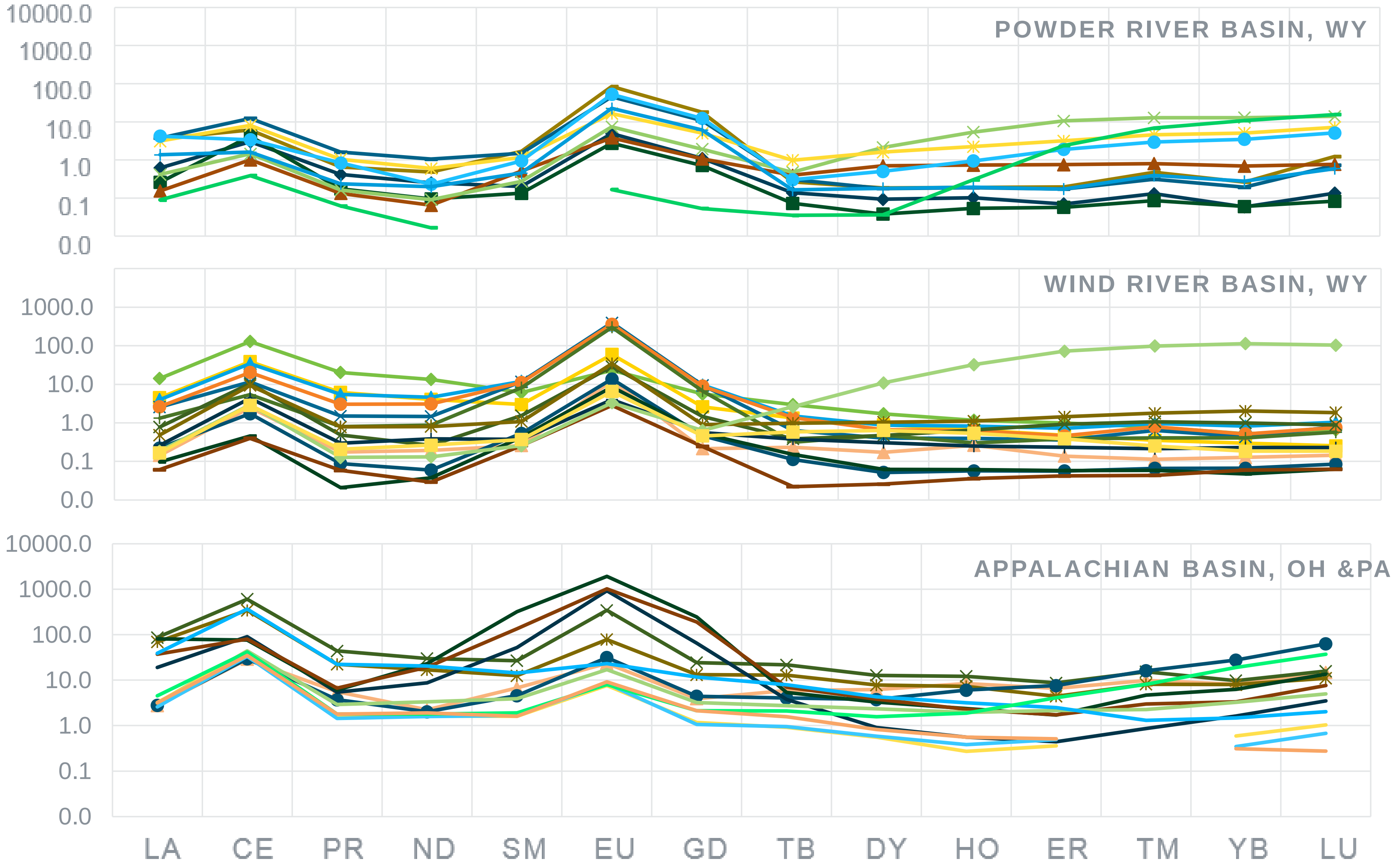

REE character of O&G Thermal Waters

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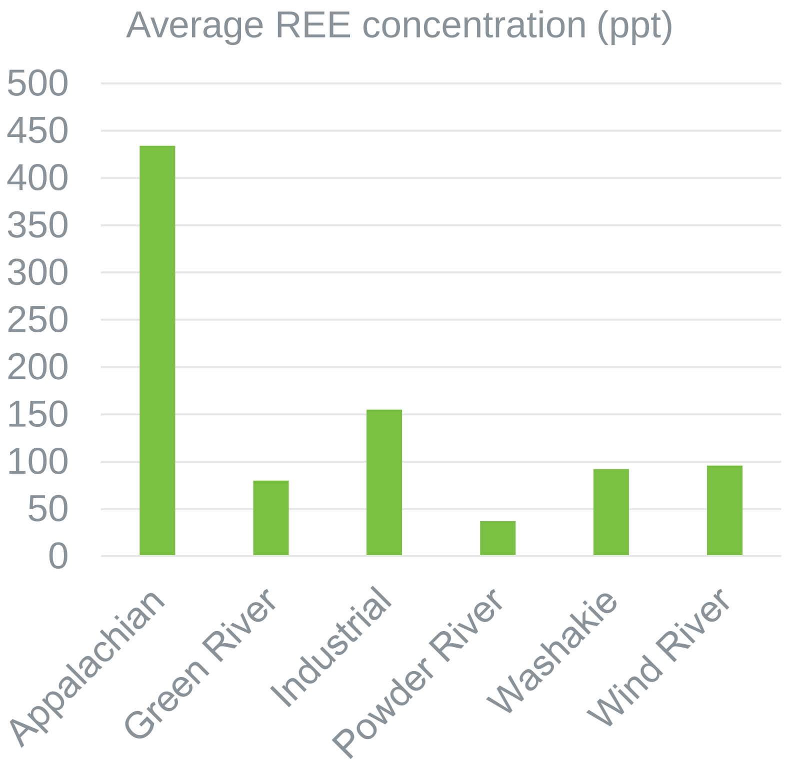
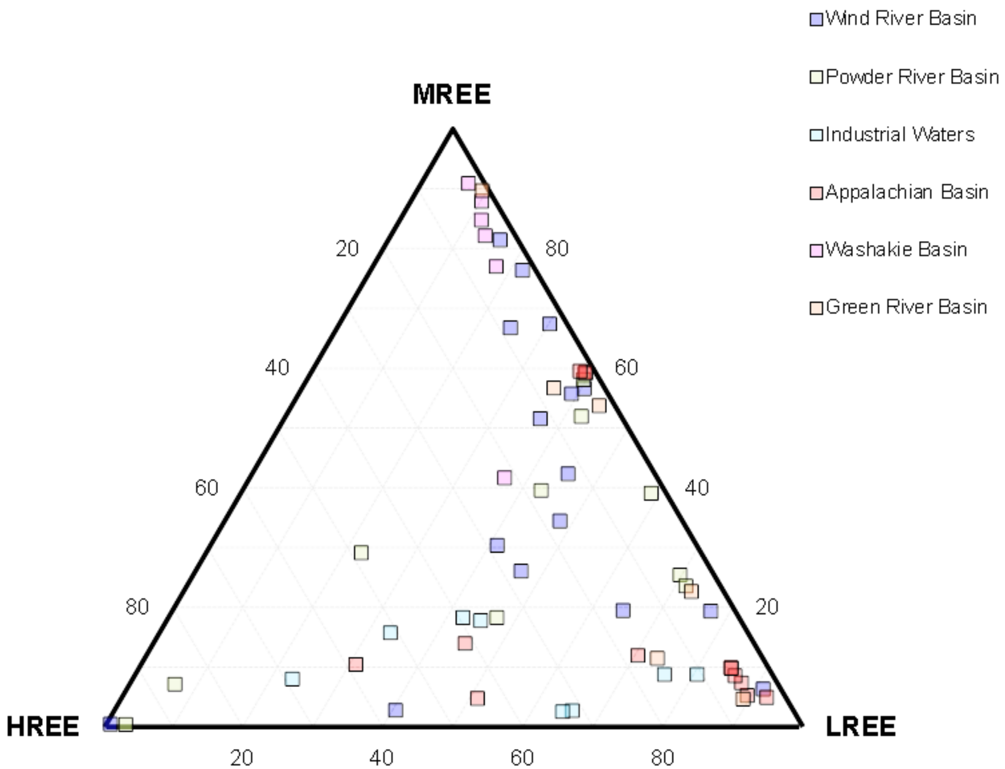


Average total REE concentration by Geologic Basin



Trilinear diagram showing the relationship of heavy (HREE), middle (MREE) and light (LREE) REEs

T3-Characterize rock associated with thermal waters

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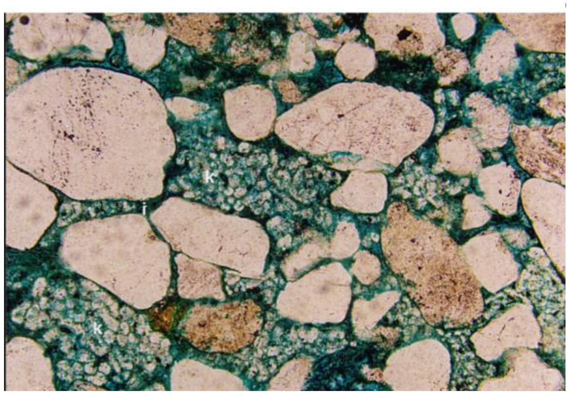
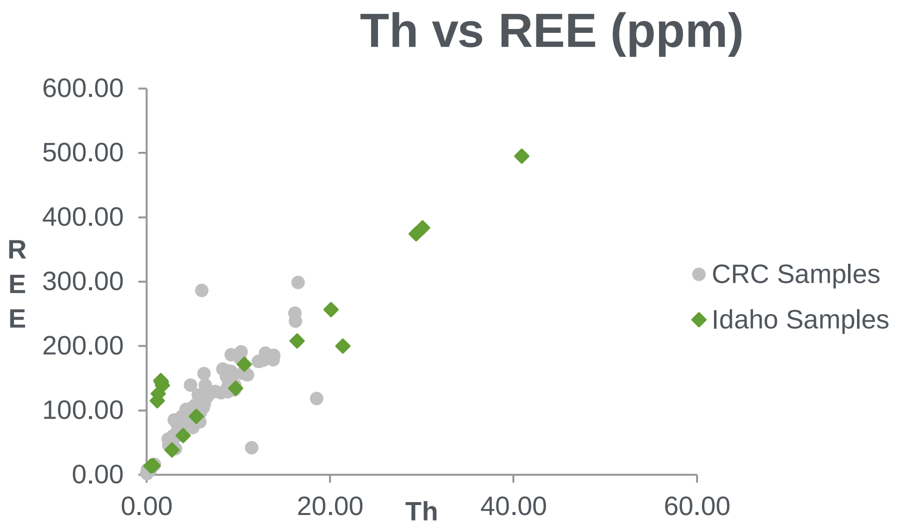
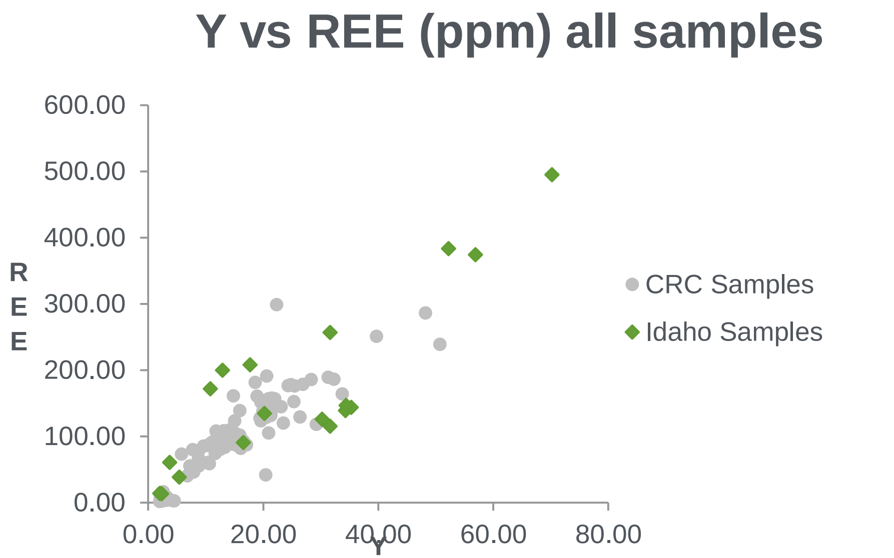
- **Goals**: Quantify host rock samples in contact with targeted REE waters
- **Action:** Analyze bulk rock geochemistry, mineralogy, and cation exchange capacity
- **Product:** Data used to identify reservoirs, and associated mineral types, with the highest potential for



Fluvial sand, Upper Cretaceous Fort Union Formation

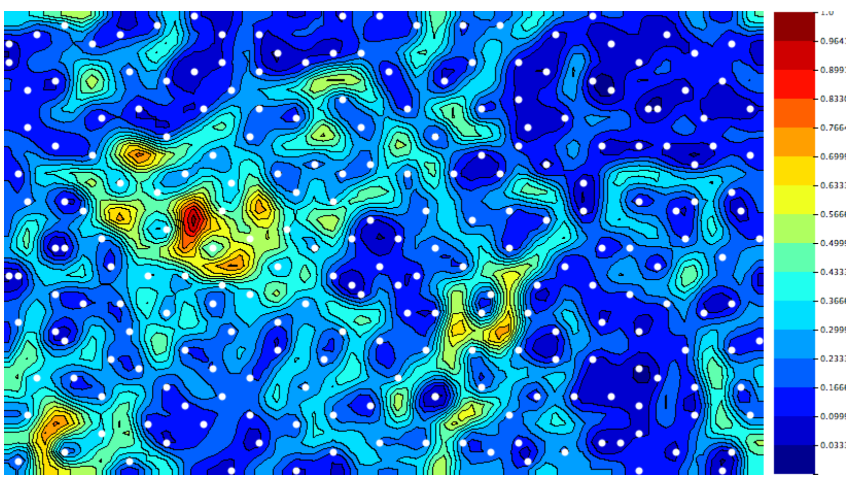




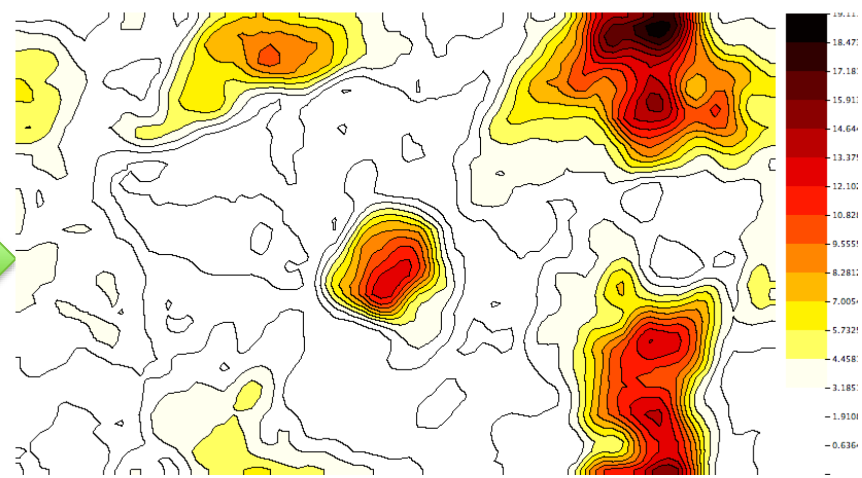
Preliminary data suggested Th/REE and Y/REE correlations in the reservoir rock

Task 5 Geostatistical analysis of REE distribution (USGS)

- **Goals**: Study possible controls on REE distribution and predict additional areas of high REE potential.
- **Action:** Build an emergent self organizing map (ESOM) is a highly adaptive form of neural network well suited for separating very complex sample groups and showing the topology of those groups.
- **Product:** The neural network will tolerate incomplete datasets and identify promising regions for subsequent REE studies.



U matrix – warmer = larger distance



P matrix – warmer = cluster center

Summary of technical accomplishments (10/8/2017)

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- 175 produced water and thermal water samples identified for REE analysis
- 143 water samples meet minimum volume requirements and were shipped to INL for REE analysis
- The creation of a robust REE produced waters dataset that represents 25 geologic formations, and multiple reservoir types (carbonate, clastic, marine, eolian, etc.), produced water types, depths, temperatures, flow rates, etc.
- 90 water samples, to date, have been completely analyzed, including all of the OGTWs.
- These data have been provided to the USGS for the neural network analysis (T5)
- Geochemistry and isotopic work on all new collected samples is complete.
- 88 analogous reservoir rock samples have been identified, collected and analyzed for REE and geochemistry
- 10 submissions to the GDR including datasets (3), technical reports(3), and paper/presentation materials (4)

Millstone	Variation	Data Completed
1.1 identify which existing samples to use from USGS Catalog	No variation	9/30/2016
1.2 Process, split and transfer of existing samples	Extended time required	5/1/2017
1.3 identify available corresponding rock samples	No variation	3/1/2017
1.4 Complete report and inventory data upload to the GDR	No variation	6/30/2017
2.1 Complete geochemical analysis of water samples and upload to GDR	No variation	6/30/2017
2.2 Format OGTW data into provided templates and upload to the GDR	No variation	6/30/2017
3.1 Rock samples collected and analyzed	Extended time required	4/5/2017
3.2 Complete geochemical analysis of reservoir rock	No variation	6/30/2017
3.3 Format and upload reservoir rock data	No vairaion	6/30/2017

Research Collaboration and Technology Transfer

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Academic Engagement

Direct

- University of Wyoming-INL-USGS
- Undergraduate Research Projects (2)
- PhD student (1)
- Presentations at professional meetings (6)

Indirect

- Extra samples provided too:
  - University of Kentucky for use in the DOE US/China CERC program
  - UW-Chemical Engineering for microbial characterization
- Collaborating with NETL to further the REE work on sedimentary rocks

Industry technology transfer

- All companies involved in the new sampling effort were provided with the data from those samples.
- Two companies have expressed interest in collaborating on field-scale REE characterization. Agreements are under review.

Future Directions

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Future work will focus on Task 2, 5 and 6

No variation is expected from the milestone list below.

Millstone	Status	Estimated Completion Date
2.3 Complete flow rate and temperature data collection	Data is bieng collected from the WOGCC	10/30/2016
2.4 Complete geochemical modeling to inform geologic interpretation	Work is ongoing	2/28/2018
5.1 Generation of a trained ESOM, using REE data	Data shared with USGS to begin ESOM analysis	10/30/2016
5-2 Complete mapping of pre-existing data to trained ESOM	Not started	2/28/2018
5.3 Collect and analyze a minimum of five samples to validate ESOM	Spring 2018	4/30/2018
5.4 Upload report including all supporting data, maps and graphs to the National Geothermal Repository on potential OGTW reservoir types and geologic regions with respect to REEs.	Maps and data are being compiled as the project progresses	6/30/2017
6.1 Economic and sustainability models complete and upload report data to the DOE-GDR in accordance with the DMP.	Literature review of available technologies	1/31/2018
6.2 Upload data and report to the National Geothermal Repository on evaluated technologies for REE separation. Recommend areas for future work.	No variation	6/30/2018

Summary Slide

- REEs in Oil and Gas thermal waters can be measured despite Ba, hydrocarbon, and salt interferences. Team members have realized a 33-fold improvement in minimal sample size

- Isotopes indicate a prolonged reaction with the host rock, at elevated temperature.

- Europium is present with a significant positive anomaly (NASC Eu/Eu* >> 3) in all Oil and Gas thermal waters.

- This anomaly can exceed 40 times the nominal NASC Eu/Eu*.

- Thorium and TDS may correlate to total REE content. Further study is needed to verify this correlation.

- Most produced waters often have a higher REE concentration than ocean water.