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

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Track 1: Mineral Recovery

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This presentation does not contain any proprietary confidential, or otherwise restricted information.
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ConocoPhillips
devon
Project goal and objectives

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Type</th>
<th>Applications</th>
<th>Element</th>
<th>Type</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce⁶⁺</td>
<td>REE</td>
<td>Oxidizer and catalyst</td>
<td>Mn⁶⁺</td>
<td>Trace</td>
<td>Steel alloys and production</td>
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<tr>
<td>Co⁷⁺</td>
<td>Trace</td>
<td>Batteries and alloys</td>
<td>Nd⁷⁺</td>
<td>REE</td>
<td>Magnets and capacitors</td>
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<tr>
<td>Dy⁶⁺</td>
<td>REE</td>
<td>Magnets and minor alloys additive</td>
<td>Ni⁶⁺</td>
<td>Trace</td>
<td>Multi-purpose metal</td>
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<td>REE</td>
<td>Lasers and steel alloys</td>
<td>Pr⁶⁺</td>
<td>REE</td>
<td>Radioactive decay heating</td>
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<td>Eu⁶⁺</td>
<td>REE</td>
<td>Lighting and NMR</td>
<td>Sc⁶⁺</td>
<td>REE</td>
<td>Catalyst and lighting</td>
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<td>Ga⁶⁺</td>
<td>Trace</td>
<td>Photovoltaics and semiconductors</td>
<td>Sm⁶⁺</td>
<td>REE</td>
<td>Magnets and neutron flux control</td>
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<tr>
<td>Gd⁶⁺</td>
<td>REE</td>
<td>Neutron flux control and many alloys</td>
<td>Tb⁷⁺</td>
<td>REE</td>
<td>Magnets and lasers</td>
</tr>
<tr>
<td>Ho⁶⁺</td>
<td>REE</td>
<td>Magnets and lasers</td>
<td>Th⁶⁺</td>
<td>Trace</td>
<td>Fuel and lighting</td>
</tr>
<tr>
<td>In⁷⁺</td>
<td>Trace</td>
<td>Photovoltaic film</td>
<td>Tm⁶⁺</td>
<td>REE</td>
<td>Lighting and lasers</td>
</tr>
<tr>
<td>La⁷⁺</td>
<td>REE</td>
<td>Catalyst and glass additive</td>
<td>U⁷⁺</td>
<td>Trace</td>
<td>Fuel and ballast</td>
</tr>
<tr>
<td>Li⁷⁺</td>
<td>Trace</td>
<td>Flux and batteries</td>
<td>Y⁷⁺</td>
<td>REE</td>
<td>Lasers and steel alloys</td>
</tr>
<tr>
<td>Lu⁷⁺</td>
<td>REE</td>
<td>Medical tracer and glass additive</td>
<td>Yb⁷⁺</td>
<td>REE</td>
<td>Reducing agent and steel alloys</td>
</tr>
</tbody>
</table>

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*)

- **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

<table>
<thead>
<tr>
<th>Geologic Basin</th>
<th>No. of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Appalachian</td>
<td>19</td>
</tr>
<tr>
<td>2) Permian</td>
<td>14</td>
</tr>
<tr>
<td>3) Williston</td>
<td>20</td>
</tr>
<tr>
<td>4) Gulf Coast</td>
<td>39</td>
</tr>
<tr>
<td>5) Wind River</td>
<td>16</td>
</tr>
<tr>
<td>6) Powder River</td>
<td>10</td>
</tr>
<tr>
<td>7) Green River</td>
<td>6</td>
</tr>
<tr>
<td>8) Washakie</td>
<td>8</td>
</tr>
<tr>
<td>9,10,11) Geothermal Waters</td>
<td>33</td>
</tr>
<tr>
<td>Industrial Waters</td>
<td>10</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>175</strong></td>
</tr>
</tbody>
</table>
T1.1 Sample and analysis plan

In the Field
- 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

In the Lab
- 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

- 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

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

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

- **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
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: $\delta^1\text{D}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}_{\text{DIC}}$

- **H$_2$O**
  - $\delta^{18}\text{O}$ isotopes heavy enriched
  - Indicate water/rock interaction

$\text{DIC}$

$\delta^{13}\text{C}$ of Dissolved inorganic carbon
WRB indicate biogenic gas
Enriched signature but missing CO$_2$
Selected REE patterns normalized to North Pacific Deep Water (NPDW)
REE character of O&G Thermal Waters

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

Average total REE concentration by Geologic Basin

Average REE concentration (ppt)
T3-Characterize rock associated with thermal waters

- **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

![Th vs REE (ppm)](image)

![Y vs REE (ppm) all samples](image)
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)

- 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)

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

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 work will focus on Task 2, 5 and 6
No variation is expected from the milestone list below.

<table>
<thead>
<tr>
<th>Millstone</th>
<th>Status</th>
<th>Estimated Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>Data is being collected from the WOGCC</td>
<td>10/30/2016</td>
</tr>
<tr>
<td>2.4</td>
<td>Work is ongoing</td>
<td>2/28/2018</td>
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<tr>
<td>5.1</td>
<td>Data shared with USGS to begin ESOM analysis</td>
<td>10/30/2016</td>
</tr>
<tr>
<td>5.2</td>
<td>Not started</td>
<td>2/28/2018</td>
</tr>
<tr>
<td>5.3</td>
<td>Spring 2018</td>
<td>4/30/2018</td>
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<tr>
<td>5.4</td>
<td>Maps and data are being compiled as the project progresses</td>
<td>6/30/2017</td>
</tr>
<tr>
<td>6.1</td>
<td>Literature review of available technologies</td>
<td>1/31/2018</td>
</tr>
<tr>
<td>6.2</td>
<td>No variation</td>
<td>6/30/2018</td>
</tr>
</tbody>
</table>
• 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.