

A Nationwide Study of REEs in Geothermal and Produced Waters: Final Results

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ABSTRACT

This study sampled and analyzed water from around the United States. Activities that enhanced this work included the co-sampling of associated rock samples, the statistical analysis of the data with an ESOM, and evaluation of extraction by three promising methods. These activities led to five conclusions (1) REEs sometimes occur in continental groundwater in excess of 1000-times their seawater concentrations. (2) REEs exist as a trace (ng/L) component in all analyzed samples. (3) The traditional distinction of light (Z=57-64) and heavy (Z=65-71) REEs in rock-mineral chemistry applies to aqueous chemistry. (4) REE content is not significantly controlled by lithology, reservoir temperature, nor salinity. (5) REE concentration, both in sampled basins and neural network predictions of potential, appears to be spatially co-associated, with the basin mattering more than formation. These five conclusions have advanced the scientific understanding of REEs in subsurface geothermal systems.

These conclusions suggest that future work study three questions. (1) What is the spatially-dependent variable that controls REE concentration? (2) Does the output of the ESOM change significantly as input samples are grown in both number and spatial extent? (3) Compared with next-gen analytical techniques, under what metrics does the current method for aqueous REE analysis perform well, and under what metrics is it surpassed? Some of these questions are being investigated in new projects that grew from this work, others would benefit from government support.

1. INTRODUCTION

Rare earth elements (REEs) have found their way into our daily lives, in the form of smart phones, lighting, rechargeable batteries, and critical roles in the move towards 100% renewable energy portfolios. While these elements have a growing strategic importance in our daily lives an economic domestic resource does not exist. REEs are mined abroad in only a few countries, primarily China. This limited pool of suppliers has pushed researchers to look for new unconventional domestic sources of REEs. In addition to the lack of domestic resources, we recognize that another domestic challenge is the management and disposal of brines co-produced alongside oil and gas.

REE resources found in geothermal produced waters could increase the cost competitiveness of those energy resources while creating domestic supplies of REEs. Prior to this study few REE data were available for produced waters, and only limited data sets existed for geothermal waters. Simply, there wasn't enough information available to understand the potential of brine-based REE resources. During the course of this study we took an in depth look at rare earth element occurrence and distribution in geothermal produced waters from across the U.S. to gather the data needed to understand the REE resource potential of continental brines.

2. SAMPLE COLLECTION AND SELECTED AREAS

The USGS, and INL entered this project with existing samples from geothermal resources. These geothermal resources included the Eastern Snake River Plain (ESRP), Kevin-Sunburst Dome, the Appalachian Basin, the Permian Basin, and the Williston Basin.

In the last several years, INL has re-visited and evaluated the geothermal resource potential in the ESRP and surrounding areas using geological, geochemical, isotopic, and thermal tools (e.g., Neupane et al., 2014; Dobson et al., 2015; Mattson et al., 2016; McLing et al., 2014). These studies resulted in new samples from several geothermal features and concentration data for major cations and anions that were expected to allow estimation of deep reservoir temperatures (e.g., Cannon et al., 2014; Mattson et al., 2016).

UW expanded upon the USGS and INL libraries by sampling from four major Wyoming basins, each with a different stratigraphy and structural setting. This collection was facilitated by UW's experience of working with oil and gas operators, and familiarity with their hope for an improved method of produced water use or disposal. UW also collected samples of rock matching each Wyoming sample and Idaho lithology.

2.1 Existing Samples

INL and the USGS contributed samples to this project from their pre-existing libraries. The USGS contribution included larger-volume samples of over 100mL (n=18) which proved invaluable to iterative improvement of the INL methods, and more typical 30mL samples (n=31) which were analyzed as INL improved the extraction and analytical protocols. The USGS samples covered three basins, the Williston, the Appalachian, and the Permian. The INL contribution (n=142) focused on Idaho geothermal resources that resulted from migration of the Yellowstone hot spot over the ESRP. INL's samples were collected with awareness of the sample volume limitation of Wood 2014's method and are a much larger volume (>2L) than most samples (~500mL). Their large volume meant they could be

analyzed before method development occurred. INL’s existing collection benefited from the work of Earl D. Mattson (INL) and Thomas Wood (University of Idaho). These INL samples are described in the final report (Quillinan et al., 2019) and other publications (e.g., Neupane et al., 2014; Dobson et al., 2015; Mattson et al., 2016; McLing et al., 2014).

In addition to these libraries of physical samples, the USGS maintains a vast database of previous water quality analyses called the “National Produced Waters Geochemical Database v2.3” (NPWGD v2.3) roughly 115,000 of which were used for the ESOM (Engle et al., 2018) that featured in the second half of the project. Because this database contained less than 5 REE analyses at the start of this project, one of the project’s goals was to impute the REE concentrations to these ~115,000 samples to aid selection of future research sites. This goal was achieved, as described in Quillinan et al. (2019) and Engle et al. (2018).

2.2 New Samples Collected for this Project

Samples were collected during the project by INL and by UW. The INL contribution focused on water samples from the Eastern Snake River Plain and Kevin-Sunburst Dome areas. UW’s contribution focused on water samples from four hydrocarbon-bearing basins in Wyoming. These samples sets were accompanied by rock sample collection. In Idaho, these rock samples came from outcrops and in Wyoming the samples came from drill core held at the Core Research Center (CRC) in Golden, Colorado. The rock samples were collected by UW. The Idaho water samples were collected according to the methods of McLing et al, 2014. This resulted in over a liter of sample volume.

To ensure successful partnerships with industry, the Wyoming water sample collection procedure had to accommodate rapid collection from an unfamiliar source. While very similar to McLing et al. (2014) some modifications were made. Three field blanks showed that these modifications were insignificant, but for caution, the strict methods of McLing et al. (2014) are recommended whenever feasible. The two main modifications were in bottle preparation, and transport prior to filtration.

All samples were collected in 500mL Low Density Polyethylene (LDPE) bottles that were pre-washed with hydrochloric acid, rinsed in the laboratory with ultra-pure water (>18 MΩ-cm), and then rinsed again in the field with the sample before final collection. In two cases, where limited water sample volumes precluded rinsing in the field that final step was omitted. There was no noticeable difference between field rinsed and un-rinsed samples.

Following collection, the sample bottles were transported on dry ice in a cooler. Upon return to the University of Wyoming (a trip of less than 8 hours) the samples were frozen overnight, and then thawed, filtered, split, and acidified the following morning. Freezing was important to arrest the biologic activity that can change isotopes and reduction-oxidation sensitive chemical species. Filtering used 0.45 micron mixed-cellulose ether filter papers to remove particulate and microbes. The split allowed analysis for anions that require an unacidified sample, and also cations (including REEs) that can be better preserved in an acidified sample. The acid used for acidification was trace metal grade 69% Optima nitric acid. Only a few drops were needed to lower the pH of the samples to ~2 as measured with pH test strips.

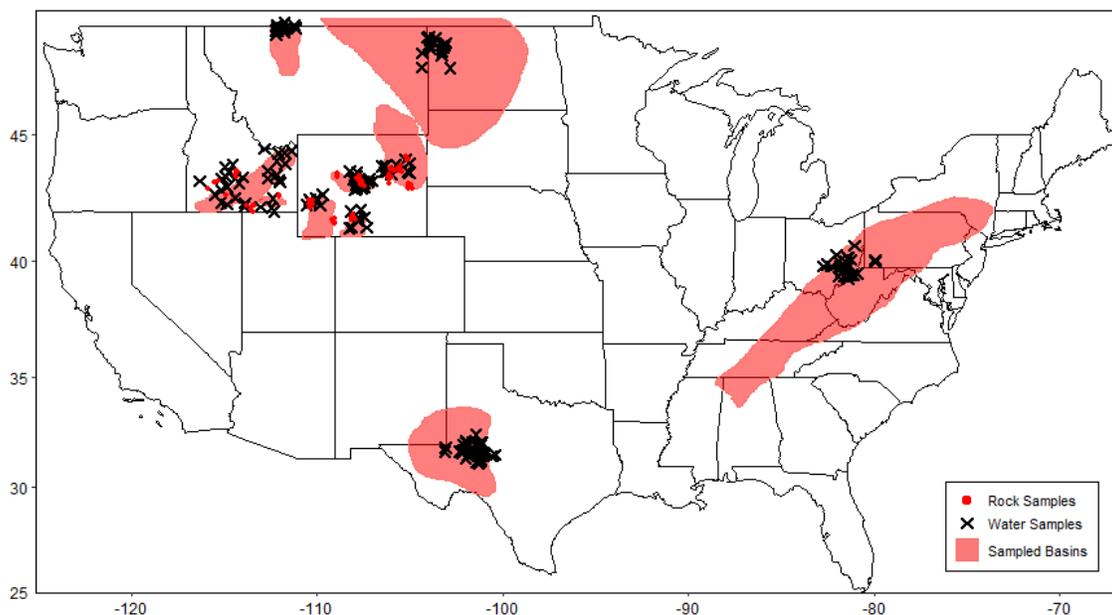


Figure 1: Basins in the United States that were analyzed for REEs in this project. The red points in Wyoming and Idaho are rock samples collected and analyzed for REEs and geochemistry during this project. The black “X”s indicate the location of water sample analyzed for REEs in this project. A jitter-function has been applied to all sample locations to show their density better.

The six areas of water sample collection were: the Eastern Snake River Plain (ESRP), Kevin-Sunburst dome, Wind River basin, Powder River basin, Green River basin, and Washakie basin. The ESRP and Kevin-Sunburst dome are described in published literature. The following sections detail the context of the other four of these locations and the general properties of their water samples. At the end of this section the USGS-provided water samples are given the same description.

2.2.1 Wind River Basin Geothermal Produced Waters, Wyoming

The Wind River Basin (WRB) is a structural basin in central Wyoming. Like most Wyoming basins, it formed in the Laramide. The basin is bounded by the Wind River Range on the west, the Granite Mountains on the south, the Casper Arch on the east, and the Owl Creek Mountains on the north. The basin’s deepest contact with granitic basement (24,000ft below sea level) occurs just south of the Owl Creek Mountains (Keefer, 1970). Samples for this project came from this area in the deepest part of the basin. There are some anomalous geothermal resources in the WRB that deviate from the expected geothermal gradient. The cause of this activity is unknown but could be related to stresses caused by the failed extreme northern branch of the Rio-Grand Rift, tertiary volcanic plugs, thermal insulation by coal seams, or blind faults that connect the deep basin to shallower units. The last option is the preferred explanation at present.

The WRB samples came from three well fields. These fields spanned shallow, hot units like the Fort Union, deeper, cooler units like the Cody, and deep very hot units like the Madison. With the exception of two holding-tank samples all samples were taken from the phase-separator.

Produced Water samples in Wyoming typically have a Europium anomaly with balanced Samarium and Gadolinium rider-peaks (Figure 2). The WRB has this style of europium enrichment. The sample set from the Lance and Fort Union Formation of the Wind River Basin (indicated by an MD prefix on Figure 2 when their source was blended) shows this anomaly in all samples. There are also samples from clastic units deeper in the Wind River Basin, and from the deepest reservoir, the Madison limestone.

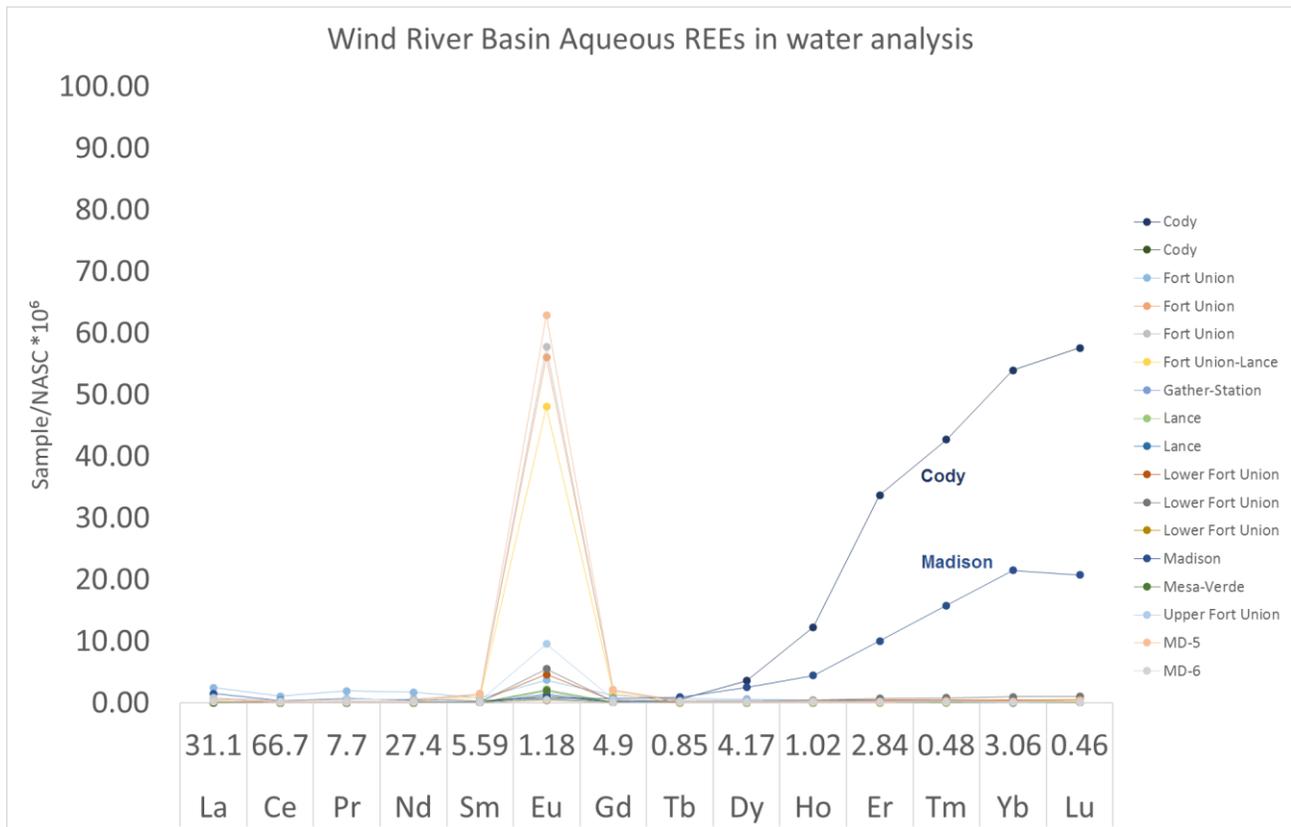


Figure 2: A NASC-normalized REE diagram for the WRB. Exempting one Cody sample and one Madison sample, there is a general but slight enrichment in LREE over HREE. The “MD” samples are gather stations that blend Fort Union and Lance.

The WRB water type in the collected samples is dominantly sodium-bicarbonate but transitions from bicarbonate to chloride with greater depths. Major cations other than sodium are virtually non-existent, as is sulfate (Quillinan et al., 2019, Appendix). The TDS of the WRB samples ranges from 3,800 to 19,100 mg/L with an outlier of 68,000 mg/L. The pH is slightly basic, averaging 7.6 units. These data are consistent with an oil and gas field in a carbonate-bearing rock system.

Europium behavior in the WRB falls into three categories: significant positive anomalies (greater than 11.8ng/L), typical positive anomalies (between 11.8ng/L and 1.18ng/L), and a significant negative anomaly (less than 1.18ng/L). The samples with a significant positive europium anomaly occur in samples from the Fort Union formation (Figure 2) which is a mature, Paleocene, continental sandstone containing significant oil and gas fields. The sample with a significant negative Eu anomaly came from the Madison limestone.

2.2.2 Powder River Basin Geothermal Produced Waters, Wyoming

The Powder River Basin (PRB) is an asymmetric syncline in northeast Wyoming possessing both stratigraphic and structural features. The basin is bounded by the Big Horn Mountains on the west, the Laramie Range on the south, and on the northeast partially by the Black Hills. The basin axis trends north-south, with a significant dip on the west limb, and a much gentler dip on the eastern limb. Samples from the PRB came from two fields, one on the basin axis, and the other on the eastern limb. Almost all modern production in the PRB is from horizontal wells enhanced with near-well rock fracturing.

Samples from the PRB are most similar to the Kevin Dome samples (Quillinan et al., 2019, chapter 4), with the exception that they have a weak europium anomaly and gadolinium anomaly (Figure 3). Two samples, from the Frontier and Mowry have minor HREE enrichment.

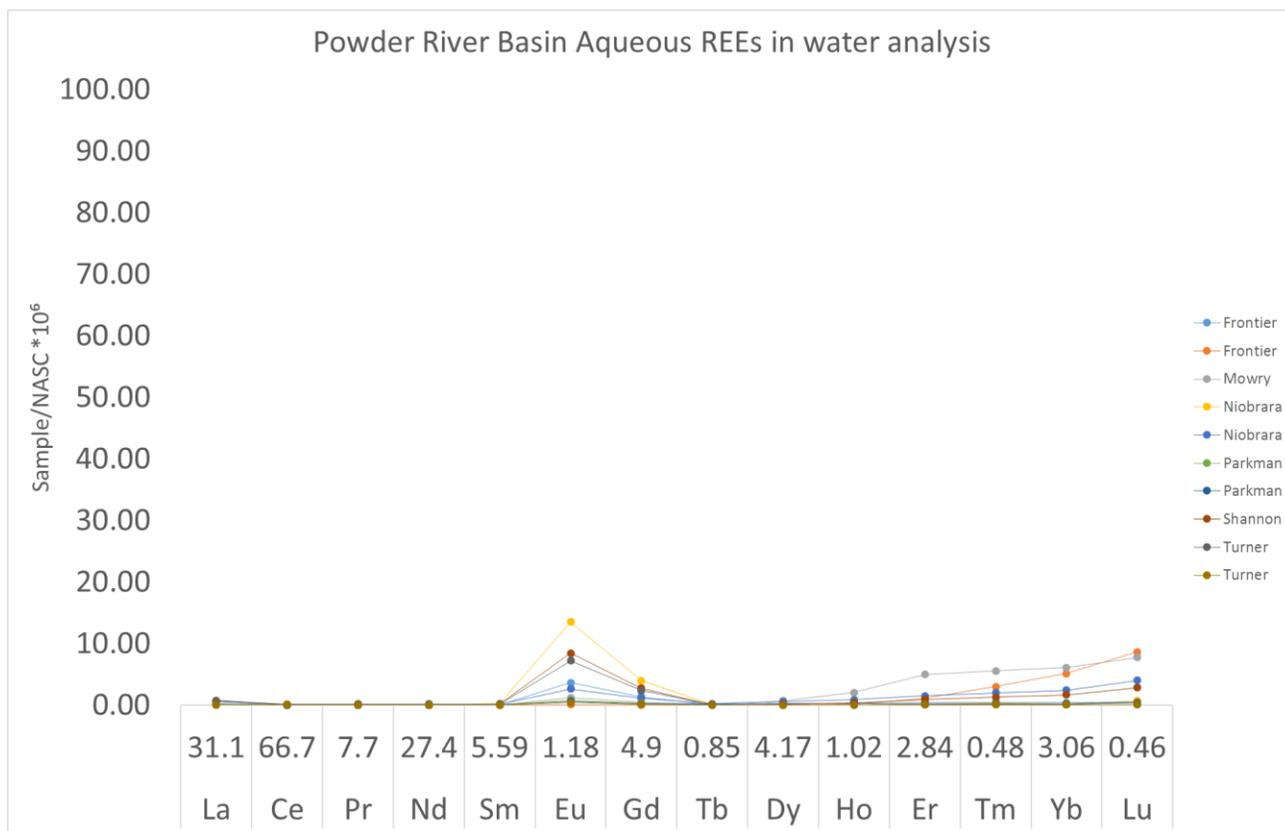


Figure 3: A NASC-normalized REE diagram for the PRB. The PRB has a small Eu anomaly. The Gd anomaly is unusual and unique to the PRB out of all samples in this project. The Mowry, one or two Frontier samples, and maybe the Shannon sample show HREE enrichment. Those four samples were collected from nearer the basin axis than the other samples. The visible europium anomaly is mostly in the typical range for produced waters.

The water type in all PRB samples is sodium chloride. The other major ions have very small contributions. Sulfate was not detected in any PRB sample. Despite being limited to an almost entirely sodium chloride chemistry, the TDS of these samples (~50,000 mg/L) is almost ten times higher than the average of other Wyoming samples. This high TDS but low REE content seen in the PRB dataset supports the conclusion of Engle et al. (2018) that TDS and REE concentration are not significantly linked. The pH of these samples is neutral.

In produced water samples with high europium content there are often small “rider” peaks on either side for samarium and gadolinium. However, in the PRB the europium is below the level these riders are normally seen (compare with the high europium WRB samples). Further, the gadolinium rider is much larger than the samarium rider.

The four samples with elevated HREE were from wells on the basin axis, whereas the other samples were from the eastern limb of the basin. These four wells may have contributions from waters further south in the PRB (that traveled along the axis), or from the western

limb (whose strata dip more steeply). A more southerly flow path would mean that the water reaching these middle-basin wells has had a greater exposure to the cretaceous host rocks and explain how the waters picked up more HREEs than the other PRB samples.

2.2.3 Green River Basin Geothermal Produced Waters, Wyoming

The Green River Basin (GRB) is distinguished from the Greater Green River Basin (GGRB) in this work. The Greater Green River Basin refers to the combined areas of the Green River Basin, Great Divide Basin, and also the Washakie Basin (see subsection 2.2.4). The Green River Basin is a structural basin in far western Wyoming. The GRB is bounded by the Wyoming fold-and-thrust belt on the west, the Uinta mountains on the south, partially by the Rock Springs Uplift on the east, and the Wind River Range on the north. Water samples for this project came from two fields in the northeast of the GRB. This area is sometimes designated the Hoback sub-basin of the GGRB. The fields bordered the fold and thrust belt and were designed to harness the structural traps of that area rather than the less dramatic traps commonly found in the center of the GRB.

All GRB samples except the Maddison were collected from holding tanks and exhibit very poor conformance to the reservoir rocks. This is most likely due to differential oxidation causing some REEs, especially europium, to fall out of solution. Another possible cause is the iron in the tanks. This iron could be removing REEs from solution analogous to the process of Shannon and Wood (2005) who used a ferric iron co-precipitation method to extract REE from aqueous samples for analysis.

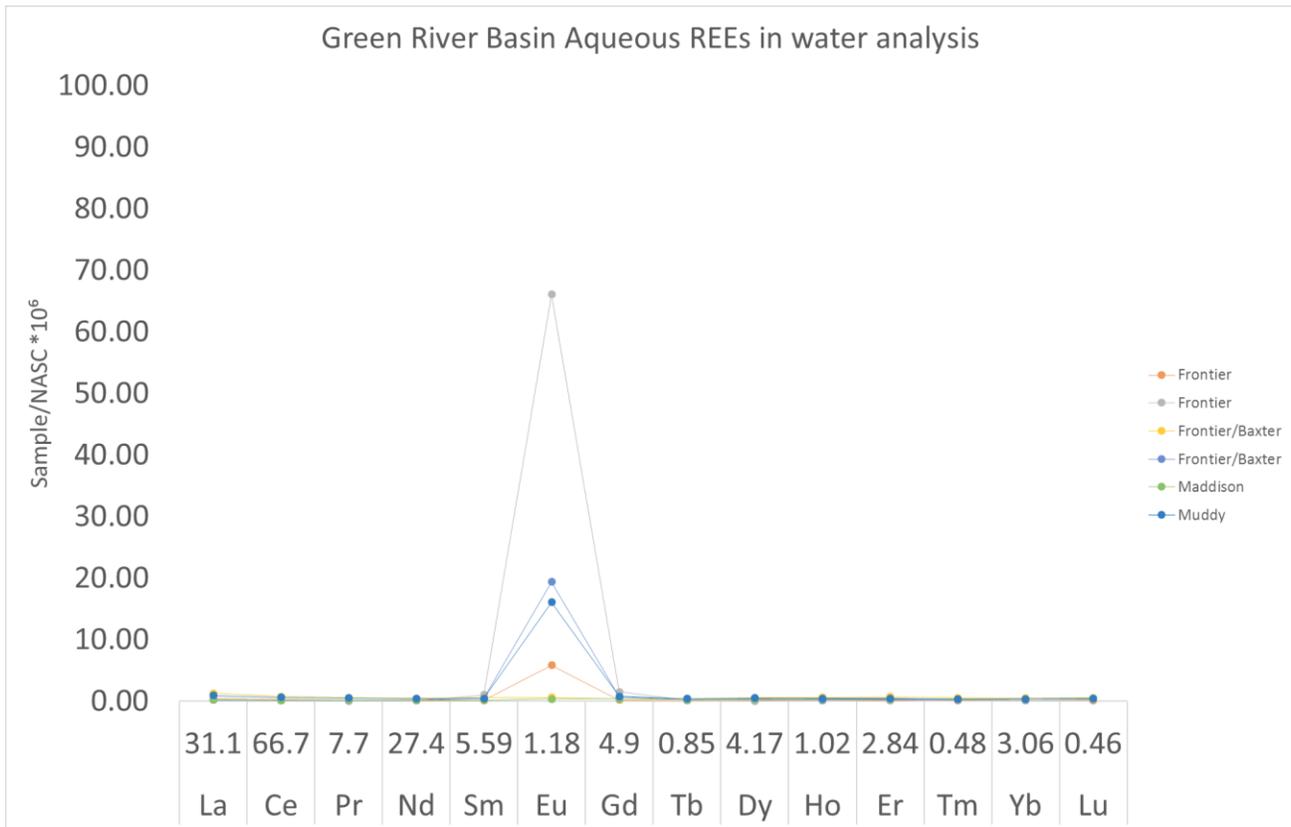


Figure 4: NASC-normalized REE diagram for the GRB. The GRB has few features at this scale. The Eu anomaly is most often small. The Frontier, Baxter, and Muddy samples which show more europium than typical for produced waters are similar to the WRB samples. Like the WRB, and unlike the PRB, these samples have balanced Sm-Gd rider peaks.

The GRB water type ranges from sodium-chloride to sodium-bicarbonate. The TDS of the GRB samples ranges from 1,000 to 20,000 mg/L, and the pH is acidic, averaging 5.6 units. These data describe a relatively clean water. However the acidic pH emphasizes that this water could scavenge elements after it leaves the reservoir formation.

The Maddison sample from this area has the same europium negative anomaly seen in the WRB Maddison sample (not shown on figure 2). However, it lacks the HREE enrichment seen in that WRB sample (4.9). The most likely explanation for this is that the GRB has less hydrothermal fluid activity to transport HREEs out of the basement rock, but that the Maddison limestone is just as deficient in REEs as in the WRB.

2.2.4 Washakie Basin Geothermal Produced Waters, Wyoming

The Washakie basin of south central Wyoming is centered around a small syncline. The basin is partially bounded by the Rock Springs uplift on the west, Cherokee ridge on the south, the Sierra Madre on the east, and the Wamsutter Arch on the north (Roehler, 1973). The

basin’s vague borders contribute to its frequent grouping in the better delineated GGRB. The Washakie basin produces a great deal of gas and gas condensate, which sometimes made water recovery challenging. Water samples in this basin came from phase separators with the exception of one sample that came from a water-holding tank.

Washakie basin samples exhibit the same style of europium enrichment as the WRB samples. They are also similar to the GRB but without the poor-correlation to rocks which is hypothesized to come from iron interaction in the tanks. This is significant because one sample (4.12) came from a holding tank but did not exhibit the poor rock correlation seen in the GRB. That sample’s good conformance could be caused by its near-neutral pH of 6.6 or by a company-specific maintenance procedure.

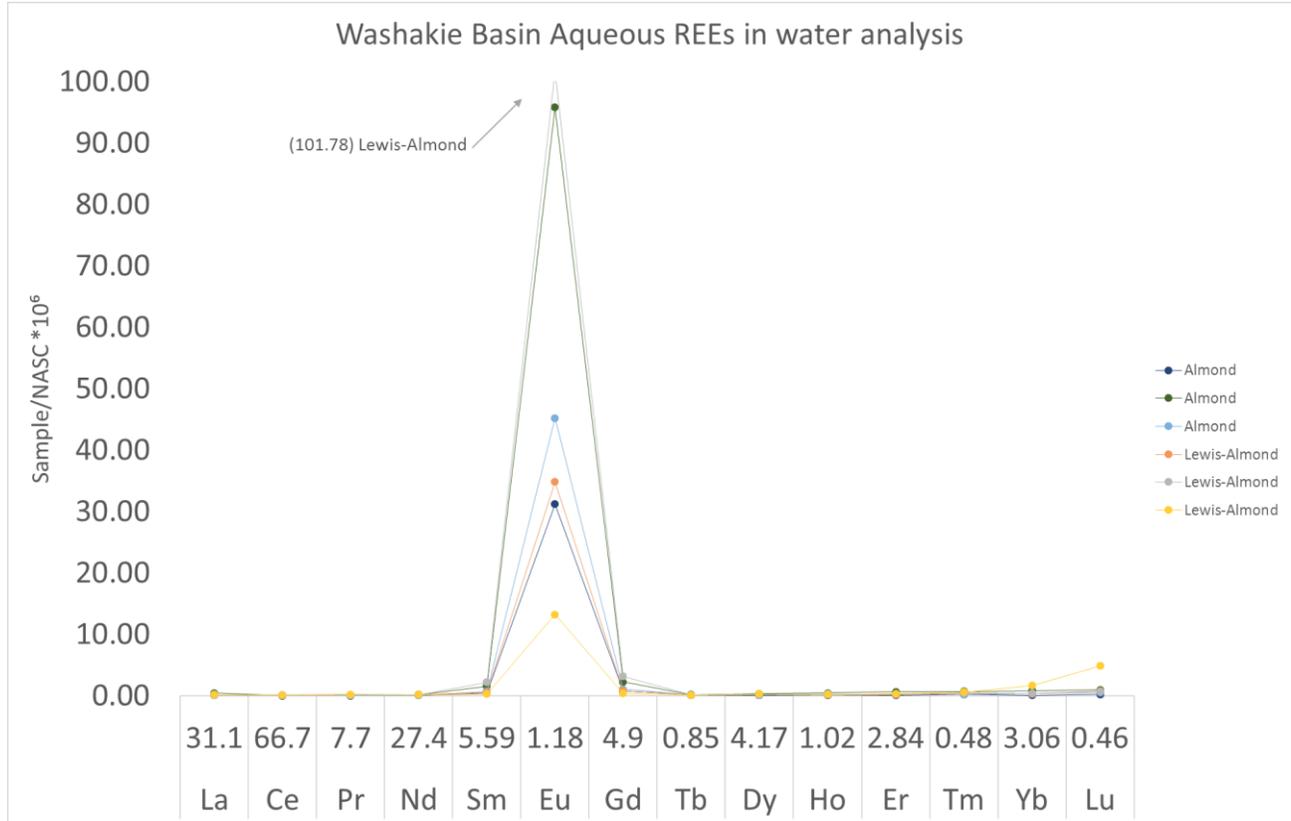


Figure 5: NASC-normalized REE diagram for the Washakie Basin. The Washakie Basin shows a pronounced Eu enrichment with balanced Sm-Gd riders. This style of enrichment is also seen in the WRB and GRB. As in those locations, this anomaly suggests a reduced water-rock environment. The low-europium sample from the Lewis-Almond, shown in yellow, was the only tank-collected sample in the Washakie. This tank sample shows HREE enrichment and better conformance to rock REEs than the tank-collected GRB samples.

The Washakie basin’s water type in the collected samples is sodium-chloride to sodium-bicarbonate but is unique among the Wyoming samples for its high sulfate, averaging 260 mg/L. The TDS of the Washakie basin samples ranges from 5,300 to 10,700 mg/L, and the pH is near-neutral, averaging 7.1 units. The general water chemistry of the Washakie is like the Wind River and Green River basins with the exception of the sulfate concentration.

A possible challenge to the conventional interpretation of the europium peak comes from comparison of these Washakie waters to their reservoir rocks Quillinan et al. (2019). The strong Europium enrichment is normally interpreted to indicate inheritance from calcic minerals (Ca-feldspars and calcite), but the rock samples that hosted these fluids are low in calcium. Nye et al. (2018) cites the oxidation-reduction-potential (ORP or Eh) of the Washakie waters and the vanadium enrichment of the associated rock as evidence that the samples from the Washakie basin were so strongly reducing that they removed europium from untraditional non-calcic minerals.

The HREE enrichment in the Washakie basin tank-sample is limited to ytterbium and lutetium. This limitation to two elements suggests that the enrichment is from a source not found in other basins, whose HREE enrichment is evident in more elements from Tb to Lu. Company specific maintenance procedures remains a possibility, or it is possible that the Lewis and Almond contain a local Yb-Lu mineral not found in other basins.

2.2.5 Williston Basin Produced Waters, North Dakota

Samples from the Williston basin partition into two distinct groups of typical LREE concentrations, and elevated LREE concentrations. Most samples have significant europium anomalies with balanced Sm-Gd riders. However there are exceptions to this both in the low-europium samples and in a minority of peaks with unbalanced riders.

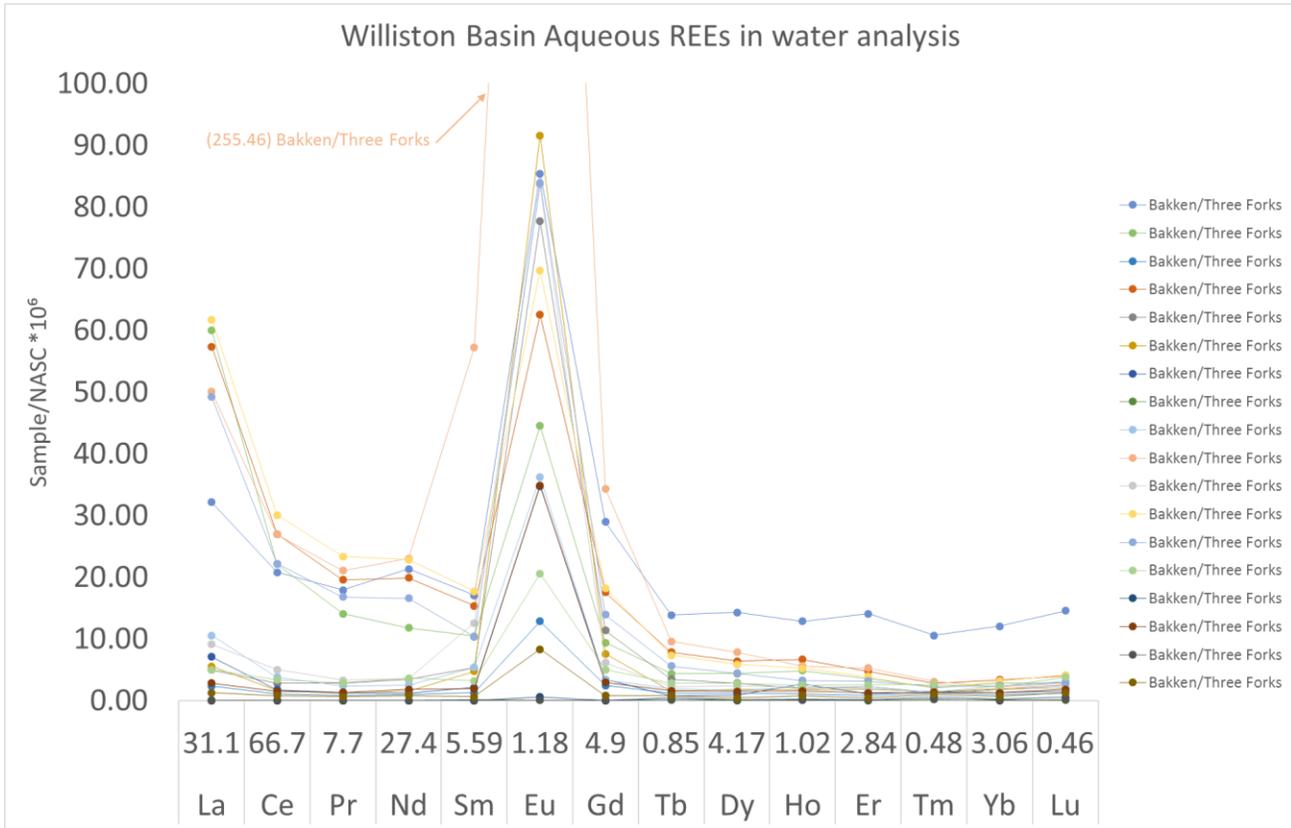


Figure 6: The Williston basin sample set shown on a NASC-normalized plot. The Williston Basin contains two distinct groups of waters defined by an elevation of LREEs or lack thereof. The most significant peak (orange) appears to have unbalanced rider peaks different from all other samples, with Sm over Gd rather than Gd over Sm. However, the samarium was most likely boosted by the LREE enrichment, so this unbalanced style is less severe than it appears.

The Williston basin, produces hydrocarbons from horizontal wells fracked in the Bakken shale. These wells are the most saline in this study with an average TDS of over 310,000 mg/L and no significant outliers. As with most wells of such high salt content their water type is sodium-chloride, and other major ions are significant. Due to sample limitations, bicarbonate was not measured in these samples, so the TDS could be even higher. The pH is slightly acidic, averaging 7.2 units with no outliers.

Shortly after REE analysis, the researchers performed bivariate analysis to learn if the high and low LREE groups correlated to any other analyses' concentration. Because no correlation was discovered, either the cause of this behavior is multi-component or depends upon on some other parameters that were not measured for these brine waters. The conclusion of Engle et al. (2018)'s advanced statistical techniques suggests that a multi-component analysis does not explain the behavior, and an unknown variable dictates REE concentration.

The unbalanced riders reflect the enrichment of gadolinium in excess of what would be expected from its nearest reliable neighbors samarium and terbium (europium is highly variable for unrelated redox reasons, and therefore not a suitable point for comparison). The gadolinium enrichment was observed in select Appalachian waters, and all PRB waters. The extensive cretaceous marine influence in the PRB is well established. Similar marine influence could have existed in Paleozoic marine shales such as the Bakken, Marcellus, and Utica.

2.2.6 Permian Basin Produced Waters, Texas

The Permian basin contains three units of interest, the Leonardian carbonates, the Wolfcamp-Cline shales, and the Pennsylvanian carbonates. Unlike the water samples from carbonate reservoirs in Wyoming that less Europium than expected, carbonate-hosted waters from the Permian basin have significant europium. Further, the two high-europium Leonardian samples also contain high concentrations of barium (more than any other carbonate in this study), but the importance of this co-variance is unclear.

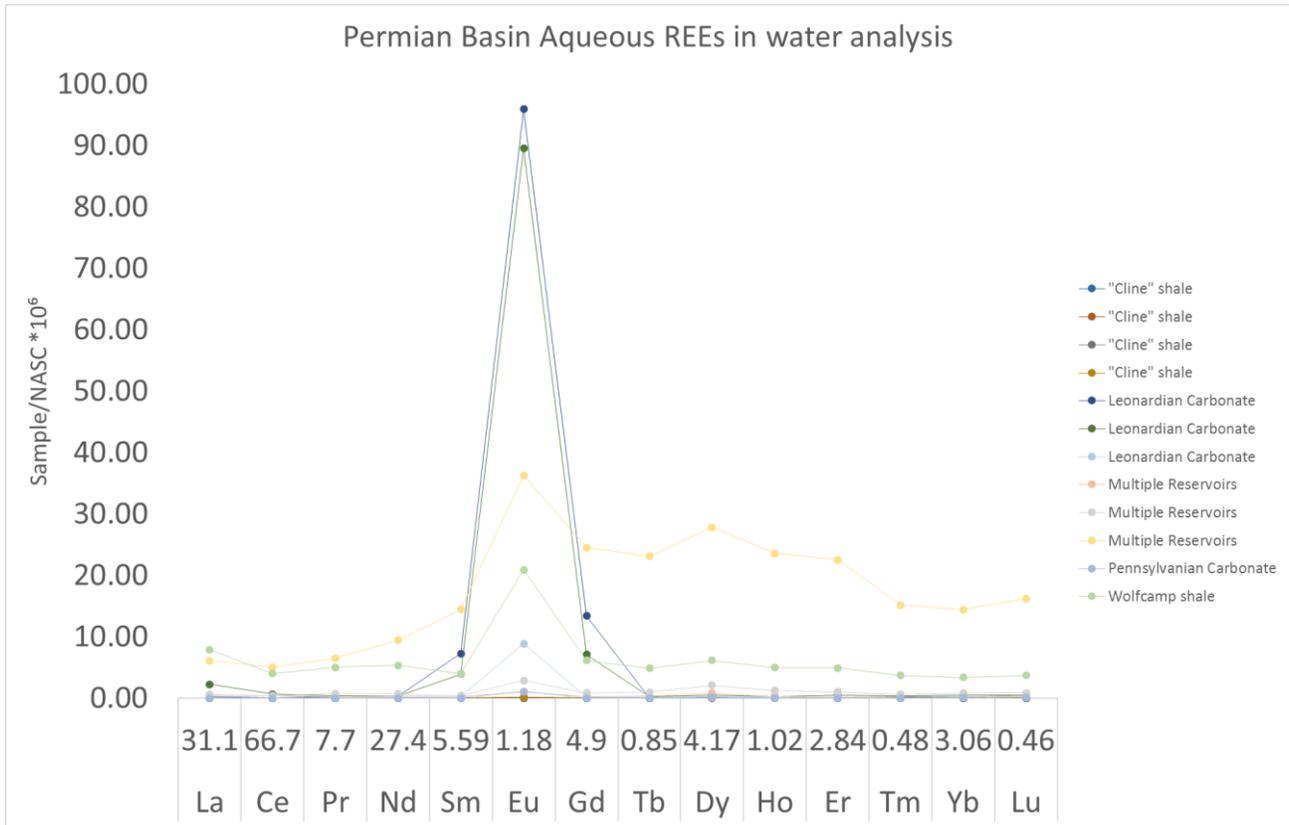


Figure 7: A NASC-normalized REE diagrams for the Permian basin. Two Leonardian carbonates have pronounced Eu enrichment with rider peaks typical of PRB-style gadolinium enrichment. The Cline samples have comparatively low TDS and are almost devoid of REEs, causing them to plot almost exactly on the zero of this graph. The yellow “Multiple Reservoirs” sample shows HREE enrichment, as does the Wolfcamp sample, to a lesser degree.

The Permian basin samples are sodium chloride type. The Cline shale samples have an average TDS of 45,000 mg/L but the other samples average 130,000 mg/L. The pH of the Permian basin waters is slightly basic, averaging 7.3 units.

The Permian basin samples contain many patterns with gadolinium enrichment. This enrichment is seen as a rider peak on the side of the europium peak. These enrichments occur most often in samples that also have high europium, such as the Leonardian, Wolfcamp, and “Multiple Reservoirs” samples.

2.2.7 Appalachian Basin Produced Waters, Eastern US

The Appalachian basin samples mostly came from Ohio, but also represent oil and gas fields in West Virginia and Pennsylvania. Like the Wyoming samples, the europium anomaly is a distinctive feature of these Appalachian basin samples. The typical Appalachian basin sample is 3 times more enriched than typical Wyoming and Idaho samples across the board.

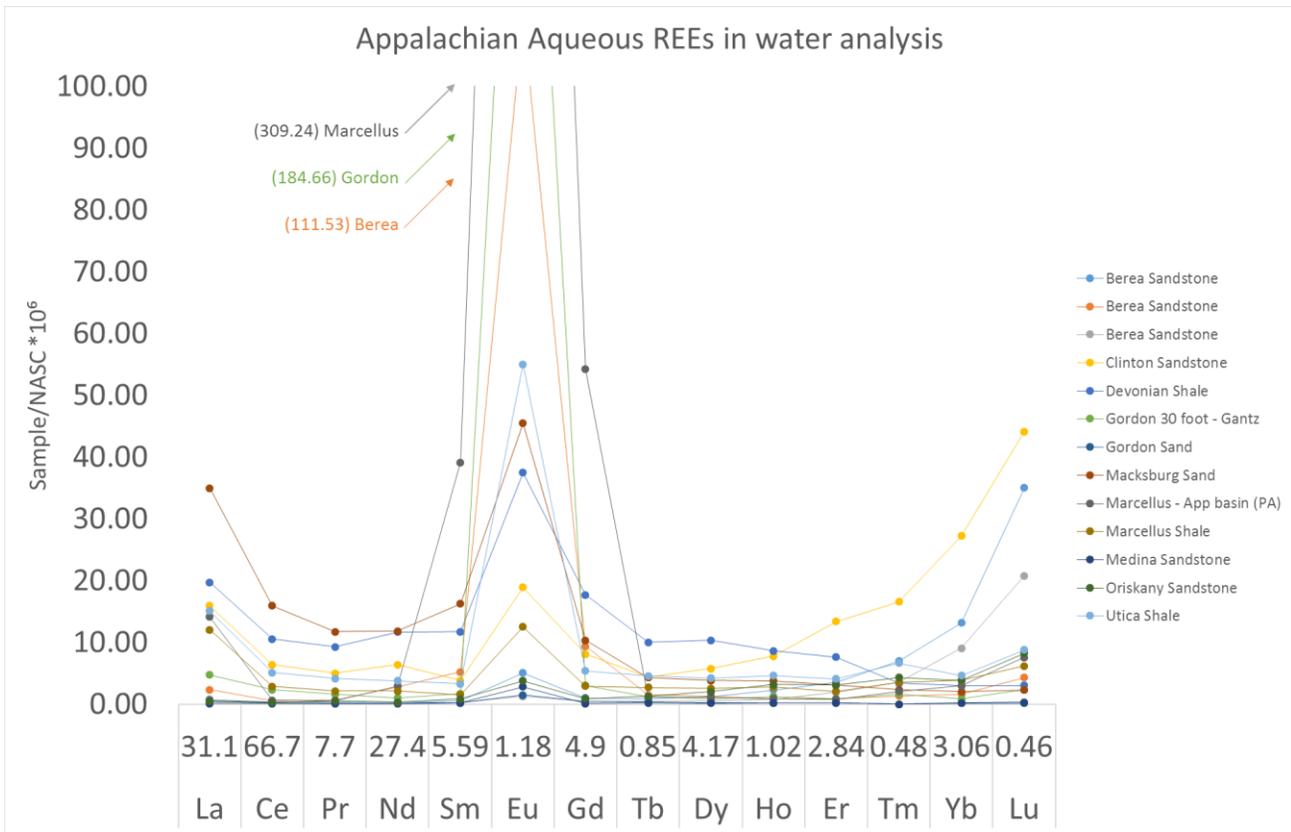


Figure 8: The Appalachian samples shown on a NASC-normalized REE diagram. The Appalachian is generally more enriched in all REEs. While some samples (Gordon sand, Medina, and Orisikany sandstones) never exceeded the typical range for REEs in produced waters (10 on the y-axis) most samples have some form of LREE, HREE, or europium enrichment beyond the expected range. The Berea sandstone (blue and grey lines) samples that have detectable but minor europium enrichment have significant HREE enrichment. Conversely, the Berea sandstone (orange line) with extreme europium enrichment has minor HREE enrichment. An asymmetry in some of the Sm-Gd rider peaks suggests a process analogous to the PRB acts on most of these samples.

The Appalachian samples are sodium-chloride type. Due to their significant TDS (averaging ~150,000 mg/L) many other major ions are present in significant concentrations. The pH is near-neutral, averaging 6.6 units. This average is distorted by the outlier pH of 4.6 found in one of the Berea sandstones (orange line in Figure 8). The acidic pH of that Berea sample could be the direct cause of its europium enrichment, but if so, further work is needed to explain why HREEs weren't similarly affected.

3. RESULTS

The study has five main results. (1) REEs sometimes occur in continental groundwater in excess of 1000-times their seawater concentrations. (2) REEs exist as a trace (ng/L) component in all analyzed samples. (3) The traditional distinction of light and heavy REEs in rock-mineral chemistry applies to aqueous chemistry. The team identifies an unambiguous, and observationally substantiated, break of light and heavy REEs in natural aqueous systems between Gadolinium and Terbium. (4) REE content is not significantly controlled by lithology, reservoir temperature, nor salinity. (5) REE concentration, both in sampled basins and neural network predictions of potential, appears to be spatially co-associated. These five conclusions have advanced the scientific understanding of REEs in subsurface geothermal systems.

3.1 REEs can Exceed Seawater Concentrations by Three Orders of Magnitude

Seawater has been suggested as a feedstock for valuable materials since before Davies (1964). The idea has been through a sequence of revivals, pilots, and in some cases economical operation such as magnesium (Lieberman, 2000) and bromide (Matthai et al. 1957) extraction plants in the United States. A common threshold for assessing the promise of an aqueous mineral resource is to compare it to seawater because the minerals dissolved in seawater are a functionally inexhaustible resource and ocean water mining technologies are direct competitors to the techniques used for continental water mining. If a resource fails to have concentrations greater than seawater it is unlikely to be economically viable barring a significant extra-market benefit, such as serving as a value-added revenue stream to geothermal energy operators.

REEs in produced waters pass this minimum check on economic viability because they can exceed seawater concentrations by three orders of magnitude. However, this only means that these waters are relatively superior to the ocean, not that they are economic in

absolute terms. Further, challenges such as removal of unwanted chemical species could neutralize this benefit. A final detail that could significantly affect the economics of REE extraction is the distinctive REE ratios seen in the WBPW (Nye et al., 2018). The WBPW shows that europium makes up a much greater fraction of the REEs in these waters than one would expect based on established REE proportions in rock. This detail could be a blessing or a curse depending on market demand for europium. A site-specific analysis of REE proportions is almost certainly essential to any assessment of economic viability, and could allow commercial operations to secure only the most attractive REEs (LREEs, HREEs, and specific elements depending on market conditions).

3.2 REEs Occur in at least ng/L Concentration in all Continental Groundwaters.

Every sample that was analyzed by INL, with the exception of the field blanks, contained measureable concentrations of REEs. This suggests that as in rocks, aqueous REEs are not rare so much as diluted in a large volume. The ubiquity of REEs in groundwater suggests that the process that places REEs into solution is non-unique, and can occur anywhere in the subsurface. While brines in some locations seem clearly more concentrated than others, no brine is devoid of REEs. The dilute ubiquity of REEs suggests that under extreme enough economic drivers, any country could compete in the REE market. The ubiquity of REEs may allow cultivation of higher concentrations if, as suggested below, the variable that controls their concentration can be isolated and manipulated. In that pursuit negative evidence and positive evidence would both be beneficial. Discovery of a location with less than measureable (0.1 ng/L) concentrations of REEs would advance scientific understanding nearly as much as finding an area of anomalously high concentration.

3.3 Natural Aqueous Behavior Suggests Distinctive Behavior between Light and Heavy REEs, matching Atomic Numbers 57-64 and 65-71

Distribution and behavior of REEs fall neatly into two groups, the LREEs and the HREEs. The well-defined divide in behavior between Gd and Tb on the principle component diagram of Quillinan et al. (2019, Chapter 6) supports these categories. While the REEs are remarkable for their similar chemical behavior, the details of their electron orbital filling may explain the observed difference between Gd and Tb. Gd is the Lanthanide with the greatest multiplicity under Hund's Rule (Hund, 1925). Gadolinium's eight unpaired electrons deviate from what a simple orbital filling order would predict by occupying the 5d orbital before the 4f is full. This deviation is partially because the total pairing energy is nearly the same as the difference in energy between the 4f and 5d orbitals in the $[Xe]6s^2 4f^7 5d^1$ configuration. The result is a larger gadolinium ionic radius more like the LREEs than the HREEs (Wolfram, 2018).

This difference in behavior is also visible with conventional normalized REE plots. As the WBPW normalization (Nye et al., 2018) shows, a break between LREE and HREEs occurs between gadolinium and terbium. It is important to note that by-and-large the REEs behave similarly to one another compared to other constituents found in produced and geothermal waters. This distinction is only apparent in detail, and most processes that affect one REE affect all other REEs.

3.4 Lithology, Temperature, and Salinity do not have a Significant Relationship to REE Concentration

The ESOM's output was compared with temperature and salinity but there was no significant relationship. The rocks were grouped into as shown in (Quillinan et al., 2019, Table 5.1) however these lithologies also had no significant relationship (Engle et al., 2018). The possibility of a particular rock having a relationship to a particular water as described in Nye et al. (2018) remains, but requires understanding of each particular water-rock system and invocation of location-specific processes. Such descriptions are difficult to reduce to single parameters that allow easy comparison to the ESOM's groupings. This is part of the reason the lithology was used for comparison in Engle et al. (2018) rather than the exact rocks.

3.5 REE Concentrations are often Spatially Co-Associated

From the limited sample set available, samples from a single basin tend to exhibit REE concentrations of the same relative magnitude and there are significant differences between the various basins. This suggests there is a variable (or variables) that controls REE concentration, and that, in turn, the unknown variable is spatially controlled.

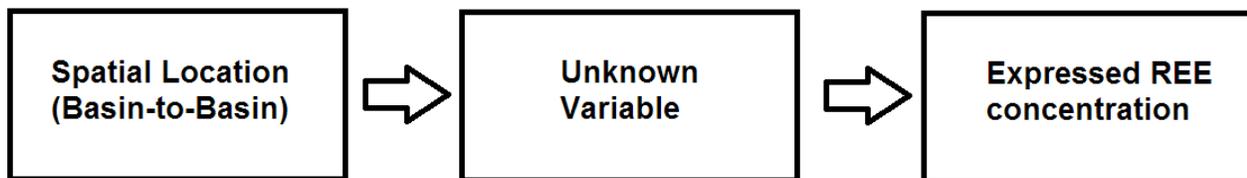


Figure 9: The sequence of causes that must exist, but is currently not known, to result in the observed spatial trends.

The expected candidate variables mentioned above do not appear to be the dominant controlling mechanisms of REE behavior, but the presence of a basin-to-basin trend suggests a controlling variable(s) exist. The variable(s), which do explain the basin-to-basin trend are of key interest for future work as in section 4 below.

The team suggests the following possible unknown variables, which were not tested in this study: (1) the rock types previously encountered on the water's recharge flow path rather than the present reservoir, (2) anthropogenic introduction of REEs or (3) in-situ microbial extraction/concentration. It is also possible that a combination of variables produces the observed REE behavior. For

example: neither marine shales nor horizontal well-construction on their own produce high aqueous REE concentrations, but when both occur together they might. This particular pair of variables has not been supported with observations during this study.

Originally the team considered that many basins could be grouped together, and that only the Powder River basin was anomalous. This view changed because the collection of new samples from more basins, and the ESOM output revealed that basin-by-basin control is the norm, and it is not only the Powder River basin that is anomalous.

4. OPPORTUNITIES FOR FUTURE WORK

The conclusions of this work suggest that future work is needed in three areas. (1) The spatially-dependent variable that controls REE concentration should be found. (2) The sample set used for training the ESOM should be grown in both number and spatial extent. (3) A comparison should be performed between the current method for aqueous REE analysis and next-gen analytical techniques. Some of these topics are being investigated in new projects that grew from this work.

4.1 Hunt for the Unknown Variable

This work established that REE behavior is not significantly correlated to TDS, temperature, nor lithology, but that REE behavior is spatially associated. This basin-by-basin trend supports the conclusion that REE concentration is non-random, and must be correlated to some unknown variable. More work is needed to discover what this unknown variable is, and why some basins, but not others, have high REE concentrations.

One option for this unknown variable is the minor components of the lithology, such as the organic fraction. This work searched for an association of major lithology components to aqueous REE concentration, but found no significant relationship. However, it remains possible that a minor component of the lithology, such as the organic fraction, could be responsible. While clastic sediments and igneous rocks are well understood, the effects of organic material on aqueous REEs need more research. Organics are well established as a good complexing agent, and strong reducing agent. Their interaction with water requires more work to understand the combined and sometimes conflicting effects of mixed clastic-organic packages on REE behavior. Clays, especially those with high ion-exchange capacities are similarly problematic.

Another option is the depositional history is more important than the unit deposited. Our interpretation of the marine Gd signature in the PRB suggests that the Cretaceous shale packages of North and South Dakota should have the same Gd behavior because they have similar histories under the Cannonball sea “arm” (Blakey, 2014). If the Cannonball sea sediments in these areas show the same Gd signature then this anomaly could be related to that event. However, if they do not show that anomaly then the entire Western Interior Seaway may be responsible for this phenomenon. While the researchers have a sample from the Bakken, shallower shale packages are not yet part of the collection, and their collection is of great interest.

Similar to depositional history, the hydrologic history of a basin may be the variable. Numerous “flushing” events have occurred in most basins, and are often associated with glaciations, which are in turn are sometimes detectable with Stable Isotope studies (Bowen, 2002). Most chemical species quickly re-equilibrate after these flushing events, but due to the lack of data on REE behavior in natural systems, it is possible that REEs do not re-equilibrate as quickly. If so, basins that have had more thorough or more recent flushing events could have different REE expressions that are out of equilibrium.

Further work should seek to rule out these candidates for the unknown spatially-associated variable or to find support for them.

4.2 Bigger Sample set that Includes ESOM-Identified Target Areas and Post-Use Waters

As with most datasets that prove resistant to interpretation, future work should prioritize expanding the dataset presented here. By adding more samples, the effect of anomalous individual samples will be reduced and the big-picture trends that affect REE behavior will begin to emerge. The ESOM’s output suggests that the geothermal produced waters of Oklahoma, northern Louisiana, southern Illinois, and the Utah-Colorado boarder should be targeted first due to their high predicted potential as REE resources. While these ESOM-identified target areas are the most likely to facilitate a better interpretation, new samples from any location might provide the evidence for a breakthrough revealing the key component of REE behavior.

Other waters that have been used for their intended purpose and then directed towards disposal could be a REE resource. These waters are typically rejected due to high salinity or unique chemistry unsuited to their continued use. Example waters include; the concentrate produced by water purification plants, cooling water that has been concentrated by evaporation with each re-cycle, water used for industrial processes such as the Solvay trona-production process, and the water used to transport coal power station ash to holding ponds. Each of these, and other post-use waters, has a different chemistry and assumedly different REE patterns. If enough post-use waters are tested, the law of averages dictates that at least one will be enriched in the most valuable REEs, and prove readily extractable. Figure 10 shows some data from a different project sampling industrial reject water sources. In this case, power station combined-ash holding ponds have more HREEs than one would expect. The sample named “Site 23” shows that by selecting the correct part of the pond a recovery operation could acquire a feedstock with significant concentration of HREEs, in an otherwise low TDS water. This expansion of the sample set into other basins will not only control noise, but also may reveal a link to REE concentration.

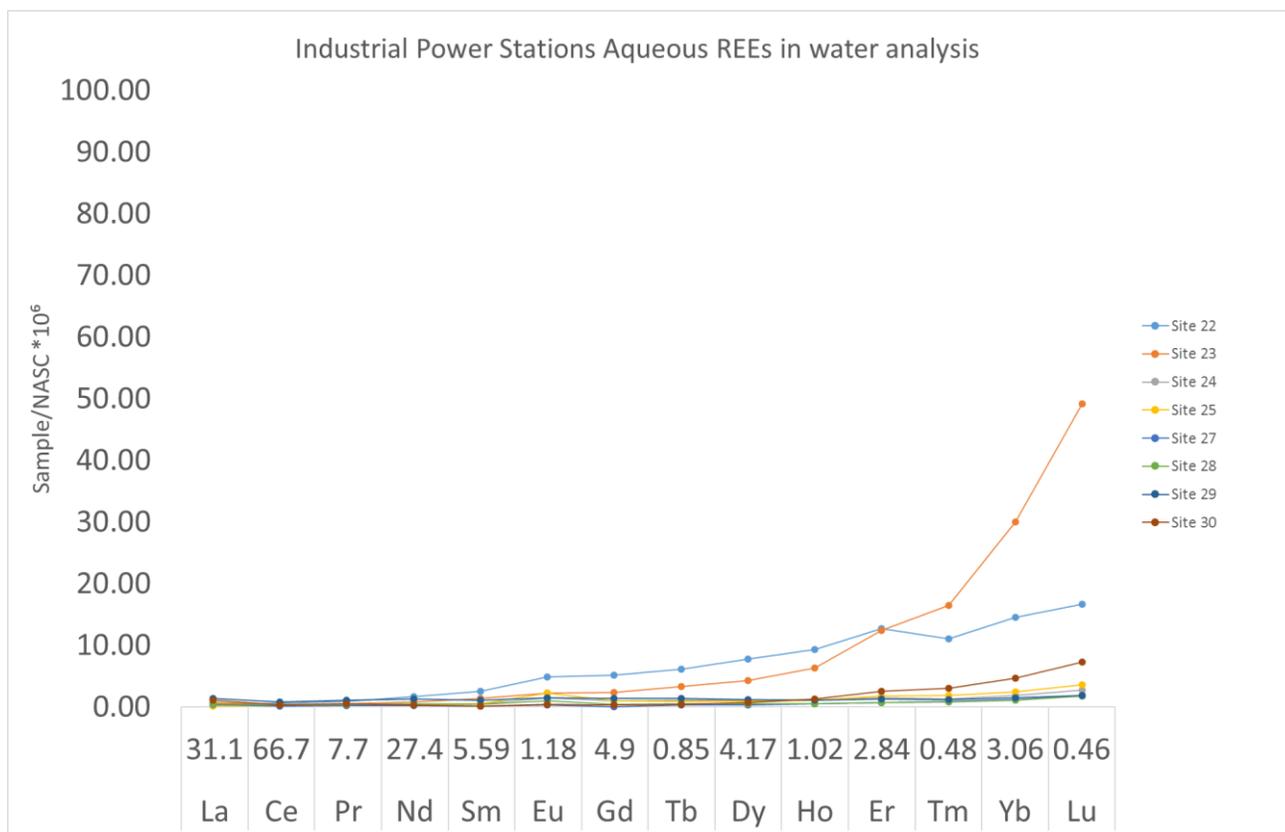


Figure 10: The REE content of water in industrial power station ash holding ponds. These eight samples are from two plants in Wyoming.

4.3 Comparison and Validation of New Analytical Techniques

In the last year next-gen analytical methods have reached the market, and some manufacturers claim they can directly measure REEs at the ng/L level without the interferences that normally render that approach unfeasible. This is an extreme claim given the long-standing historical difficulties of direct measurement, and requires cautious optimism. An option for future work is to perform a comparative analysis with a next-gen ICP-MS, such as the Agilent 8900 Triple Quadrupole, and the current pre-concentration method. Such a comparison would reveal, under realistic conditions, what areas the next-gen methods are superior, and which areas the current method is superior. This would allow other researchers to correctly choose either these next-gen methods or the current method based on the details of their work on REEs in natural systems.

5. CONCLUSION

Initial findings suggest that more work is needed to understand the dominant controls on REE concentration in geothermal and produced waters, but general characterization of REE concentrations in natural geothermal groundwater now exists. From this limited data it is not currently clear whether economic concentrations of REEs exist in these systems, but it is clear that continental groundwater offers a potentially much more abundant source than seawater. A serious geochemical exploration program would be needed to find and characterize the upper end of REE concentration in these systems. Despite uncertainty, this report presents the first step in this answering these questions. This study has shown new discoveries that enhance the scientific community’s understanding of REE behavior in natural systems. It is important to keep researching REEs in natural systems, because although many questions are now answered, many more questions remain.

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CN and GN drafted the final report (Quillinan et al., 2019) from which most of this manuscript is derived. SQ drafted the introduction and identified the sections to include in this manuscript. CN formatted those sections for flow and compiled edits. Authors of the respective chapters of the final report conceived of the work presented in those chapters. All authors reviewed the chapter manuscript. Funding for this work was provided by U.S. Department of Energy, Geothermal Technologies Office under Award DE-EE0007603. The authors would like to thank our DOE project managers Holly Thomas and Josh Mengers and also our Technical Monitoring Team for their support, advice, and insight.

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