

A New Wyoming Basin Produced Waters REE Normalization and Its Application

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Keywords: rare earth elements, REE, value-added, Wyoming, normalization, WBPW, water-rock interaction

ABSTRACT

We propose a new rare earth element (REE) normalization using 38 samples of Wyoming Basin Produced Waters (WBPW) and apply it for aqueous REE interpretation. These waters were analyzed for aqueous REEs at Idaho National Laboratories (INL) and a unimodal Gaussian fitted to the data. The result is appropriate for use with deep basin brines such as geothermal and hydrocarbon-bearing waters. The new WBPW normalization is structurally similar to North American Shale Composite (NASC, Gromet et al, 1984). However, like the North Pacific Deep Water (NPDW, Alibo and Nozaki, 1999), it is appropriate for parts per trillion REE concentrations, whereas NASC is appropriate for parts per million. The WBPW differs significantly from both the NASC and NPDW in its treatment of the redox-sensitive REEs cerium and europium. By normalizing other samples - which were not used in the calculation of the WBPW - we can show meaningful structure in REE water patterns such as those from high-temperature carbonate reservoirs. Previous work (Nye et al., 2017) noted that Wyoming's Wind River and Powder River Basins were easily distinguished by their contrasting gadolinium anomaly (Gd/Gd*). Twelve new samples from the Green River and Washakie Basins have Wind River Basin-like gadolinium behavior. These new samples suggest that the Powder River Basin is anomalous among Wyoming basins, and that aqueous Gd enrichment is less common than previously thought. This revision points to reactions with the reservoir rock being the primary factor in aqueous REE behavior, and partitions our samples into two main groups: waters from reservoirs of dominantly continental-petrogenesis and waters from reservoirs of dominantly marine-petrogenesis. Rocks from continental-petrogenesis or marine-petrogenesis appear to transfer a different Light REE - Heavy REE (LREE - HREE) behavior to reservoir water. A sub-group of three waters in the marine-petrogenesis group exhibit a unique "steep" HREE-enrichment behavior. Contributors: Yuriy GANSHIN, Travis MCLING, Ghanashyam NEUPANE, Fred MCLAUGHLIN.

1. INTRODUCTION

Researchers at the University of Wyoming, Idaho National Labs, and U.S. Geological survey have collected geothermal water samples from across the United States. These samples have been processed to remove interferences and hydrocarbons then analyzed for geochemistry, including aqueous REE concentrations. On average, the geothermal brines have greater La, Ce, Sm, Eu, and Gd concentrations than the ocean. Specific samples exceed the average ocean concentration for every REE.

A new normalization was developed because the discovered structure of continental deep basin brines is unlike existing normalizations in both concentration and morphology. This normalization was developed by fitting a single-peak Gaussian to a well-behaved subset of the samples, exclusively from the state of Wyoming. This revealed the Gaussian mean and variation in each REE. The resulting normalization, presented here as the Wyoming Basin Produced Waters (WBPW) normalization, reflects a water-rock interaction in basins charged with meteoric water on their margins. As meteoric water contains little or no ions, the water-rock reactions reflected in the WBPW are driven by equilibration with reservoir rock in either a fast-flowing open system, or slow-flow closed system.

2. DATA COLLECTION

Existing libraries and new collections by researchers at the University of Wyoming, Idaho National Labs, and U.S. Geological survey resulted in over 100 geothermal water samples for this project. Researchers at the University of Wyoming also collected rock samples from core plugs that match the reservoir rock hosting the water samples. Because those samples allow comparison of water and rock they are considered here.

2.1 Water Sample collection

Samples were collected from eight fields in four major Wyoming basins, with between 4 and 17 samples from each basin. Most samples were collected post Oil and Gas separator from sampling valves. In ten cases, where this was not possible, the samples were taken from holding tanks on the well-pad. Those ten samples represent a longer-duration average of the water produced from the wells, but are subject to more significant cooling than those samples taken directly from the separator's valves. In some cases the separator valve released a sample containing significant hydrocarbon fractions. In these cases, the sample was allowed to gravity-separate, the light-fraction removed, and the bottle refilled to gain more heavy-fraction water for analysis.

The samples were collected in 500mL Low Density Polyethylene (LDPE) bottles that were pre-washed with hydrochloric acid, rinsed in the lab with ultra-pure DI water, and then rinsed again in the field with the sample before 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 unrinsed 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 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 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.

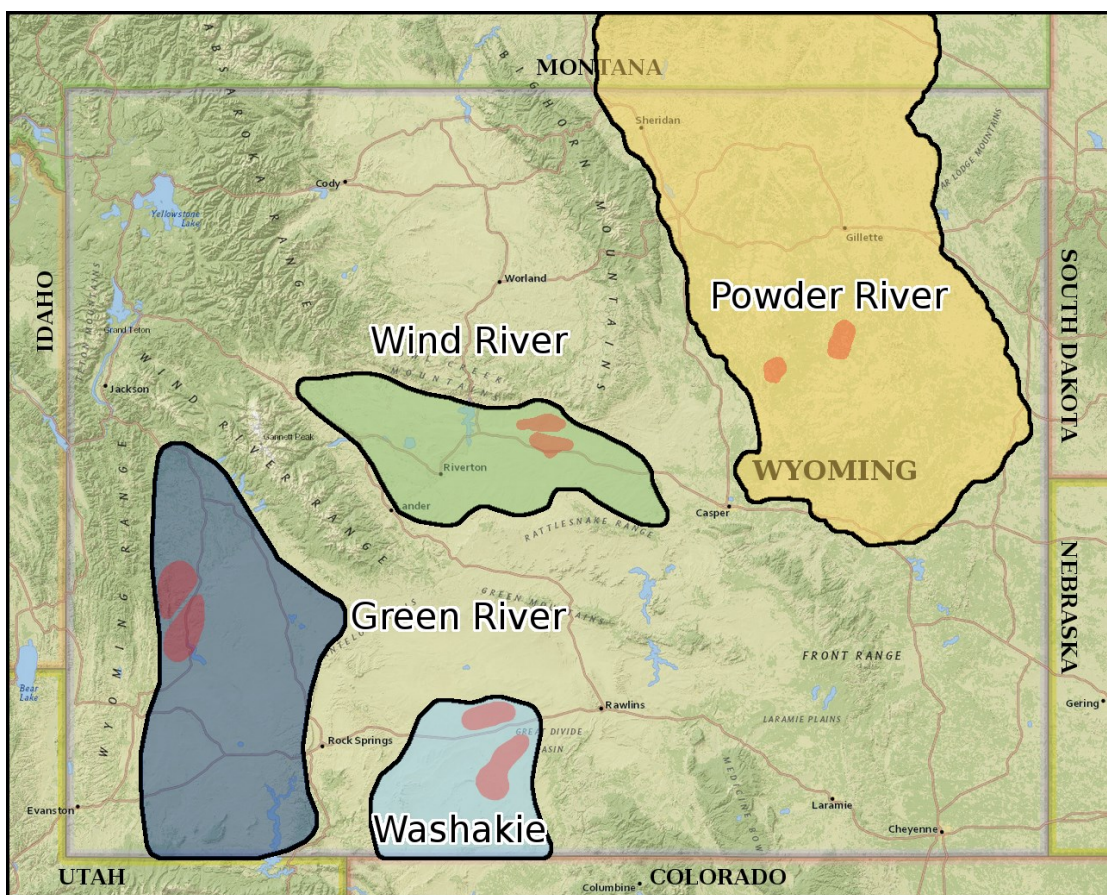


Figure 1: The Carbon Management Institute’s Wyoming dataset is spread over eight well fields (red) in four major Wyoming Basins. The dataset contains water chemistries from clastic sandstones, shales, and carbonates. The wells used for sampling ranged from 25,000feet to 7,000feet deep sometimes with conductivities of over 30mS. All of these wells that access the deep subsurface were drilled for oil and gas production, and for this reason the normalization formed from them is called the Wyoming Basin Produced Waters normalization.

The preserved water samples were stored refrigerated until analysis. This holding time was always less than a month for acidified samples, and less than a week for unacidified samples. The bottles were stored tightly capped during this time, and only opened a few minutes prior to analysis. Three field blanks were maintained during sample collection and processing.

2.2 Rock Sample Collection

Researchers at the University of Wyoming collected 83 rock samples representing target formations in 4 Wyoming basins. Wyoming basin samples were selected from core available at the USGS CRC facility in Golden, CO. Core samples were chosen as best representations of basin subsurface intervals (formation types) where water samples used in this investigation originated. When enough information about well perforation intervals was available the team attempted to match the sub-region of the formation that most closely matched this perforated interval that the waters came from.

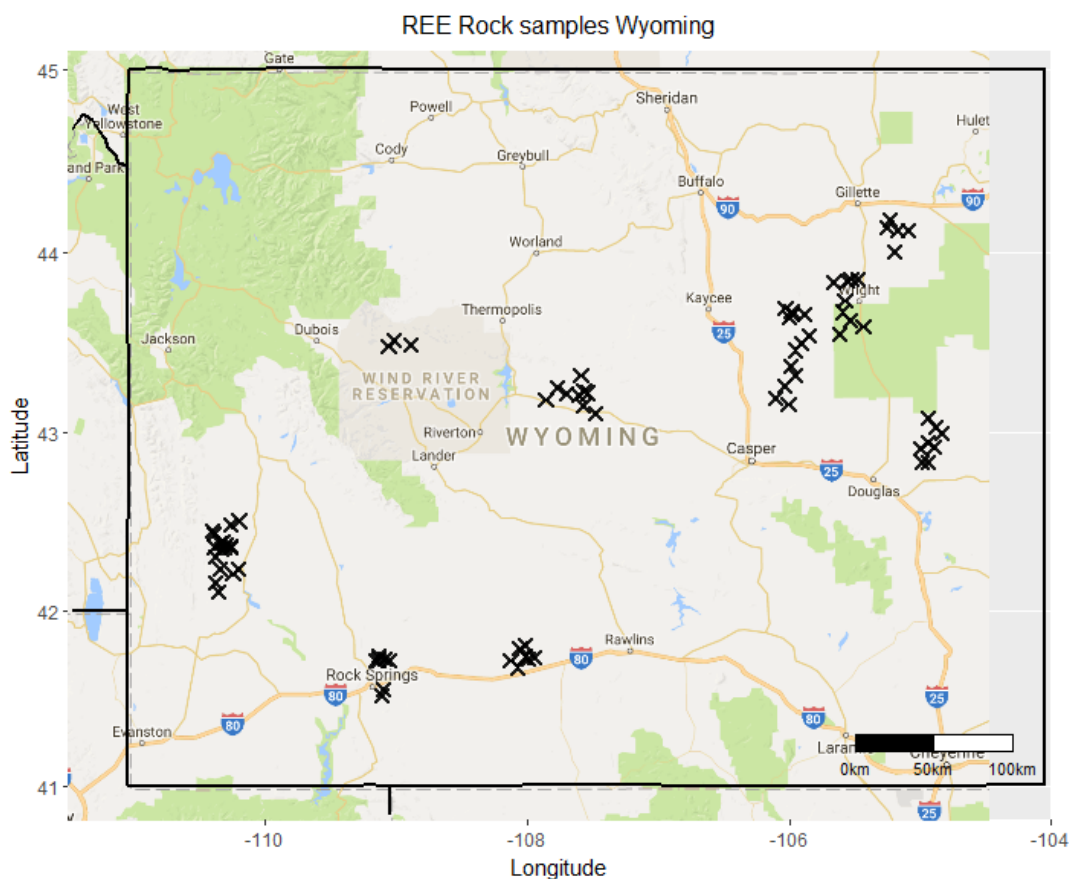


Figure 2: A reservoir rock that matched each water sample was identified for this project and collected. As seen through comparison with Figure 1 the rocks often came from core samples that matched both the location and reservoir depth.

The core plugs were split into a chunk for whole rock chemistry and a slice for thin sections.

2.3 Analysis of Water samples

Waters were analyzed with field measurements of pH, temperature, conductivity, and Oxidation-Reduction Potential (ORP). Ion Chromatography anion analysis of the unacidified fraction was used to identify monoatomic and polyatomic anions. The acidified fraction was used for elemental analysis by ICP-OES to determine cation concentration. Although not presented here, other analyses included stable carbon/oxygen/hydrogen isotopes and metagenomics sequencing. A separate acidified fraction was sent to INL for aqueous REE analysis with resin cleaning and pre-concentration under the methods of (McLing, 2014).

2.4 Analysis of Rock samples

Samples were analyzed using optical microscopy methods common to thin section petrography. Geochemistry of rock samples was analyzed by both ICP-AES and ICP-MS standard procedures for whole-rock geochemistry major oxide and trace element compositions respectively (ALS, Reno, NV). To verify trace element geochemistry, including REEs, comparison with previously obtained data for similar formations in Wyoming basins was made. Measured REEs for each rock sample were plotted on standard REE spider-diagrams normalized to the Upper Continental Crust (UCC) and North American Shale Composite (NASC) as appropriate. For example, igneous basement and clastic reservoir samples were initially UCC normalized for comparison, while shales and related sediments were compared with NASC normalizations. NASC normalization was used later for all samples in comparison to water REE concentrations, as NASC and NPDW are both marine origin derived normalizations.

3. THE WBPW NORMALIZATION

With the assistance of Dr. Ganshin at the University of Wyoming the aqueous REE concentrations of 38 Wyoming water samples were statistically assessed to fit a single peak Gaussian function to each element. The combined Gaussian means of these REEs forms the Wyoming Basin Produced Waters (WBPW) normalization. The normalization was limited to just the Wyoming samples because they have the most controlled variables, such as being collected by the same researchers in all cases, and because they have associated rocks to use for comparisons such as those in the later sections of this paper.

3.1 How the Normalization was made

This normalization was made by selecting 38 exemplar water samples from the Carbon Management Institute’s Wyoming dataset. The samples were selected for their lack of unique features, for their reservoir type, and for the quality of their analysis. First a log-histogram was formed from the measurements of aqueous REEs in each sample. Second, single-peak Gaussian Probability Density Functions (PDF) were fitted to these histograms to identify the mean concentration and variation from the mean. (Ganshin, 2017) While the confidence interval is informative and shows the greater precision in HREEs, it was not reflected in the normalization.

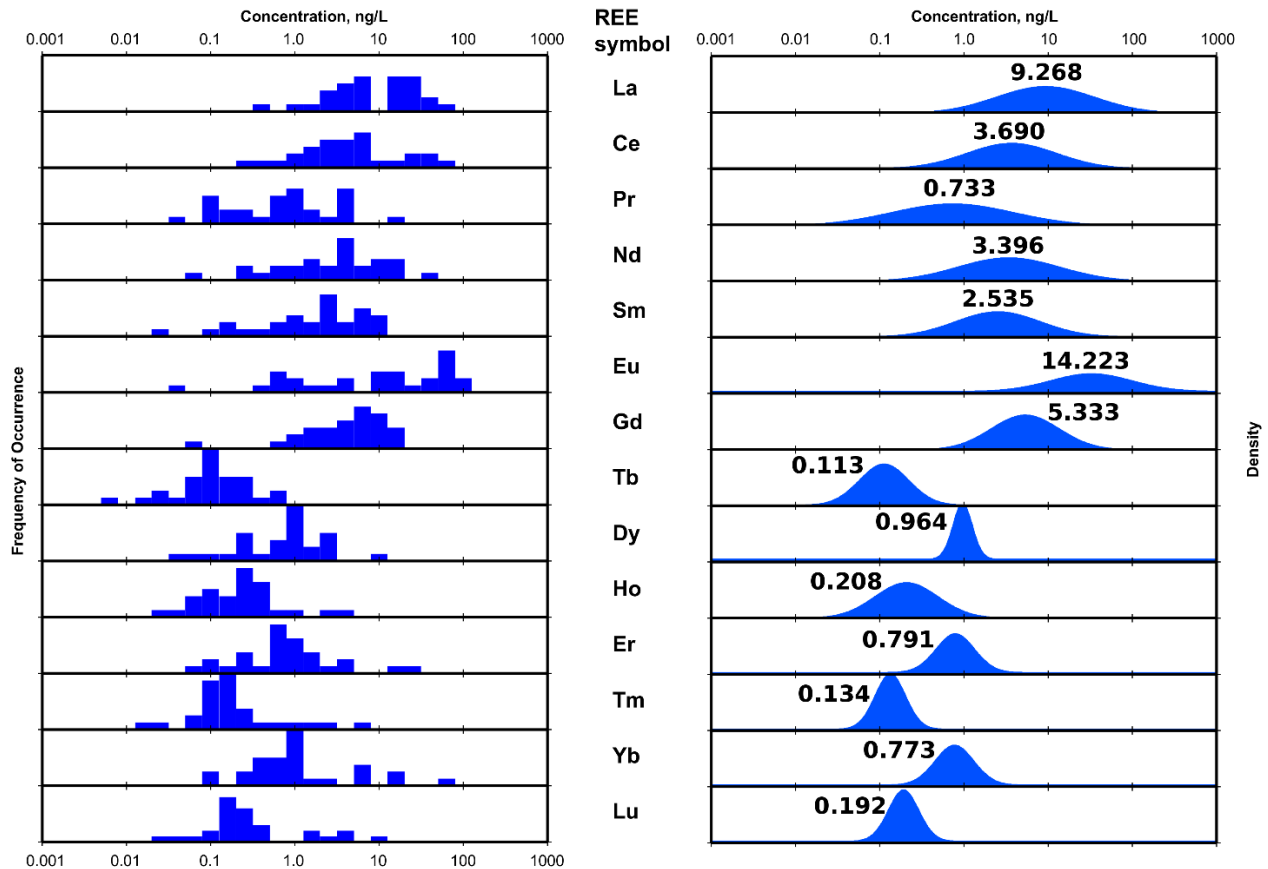


Figure 3: Empirical concentration histograms of Rare Earth Elements (REE) measured in 38 Wyoming samples (left) and the corresponding theoretical probability density functions (PDF’s) obtained by fitting empirical distributions to a mono-peak Gaussian function, (right). The numbers indicate the theoretical peak (mean) concentrations (Ganshin, 2017).

The features visible in the PDF show both the Oddo–Harkins rule, and the fractionation of LREEs over HREEs. By choosing a normalization that reflects both of these their distracting effect on the REE patterns of the waters can be removed. Future collections are expected to improve this normalization.

3.2 Features of the Normalization

As shown in **Figure 3**, we propose a new normalization to ease comparison of REEs in groundwater. Generally the LREEs were more variable and lower confidence, while the HREEs were better constrained. Also, as mentioned above the Oddo–Harkins rule and the LREE/HREE fractionation that is found in every terrestrial normalization is also present in ours.

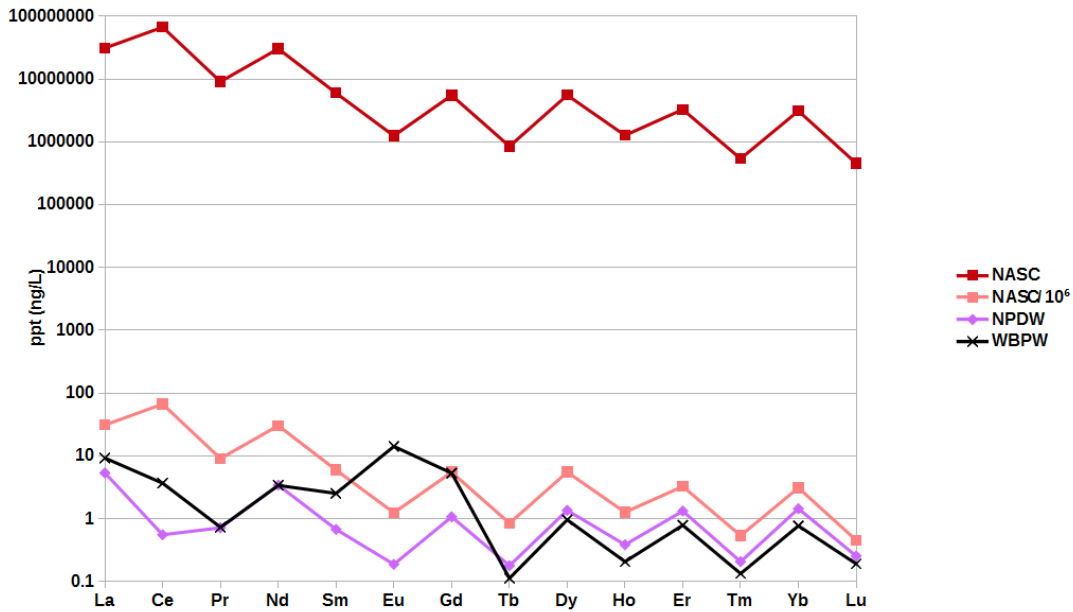


Figure 4: Chart of the absolute concentration in ppt of the North American Shale Composite (NASC in red), which has a pattern distinct from the North Pacific Deep Water (NPDW in purple). This can be seen by shifting NASC down by six orders of magnitude (pink). This difference in pattern is apparent in the Ce/Ce* concentrations, and also in the overall slope of the lines from LREEs to HREEs. We suggest a new normalization called Wyoming Basin Produced Waters (WBPW in black) which better matches on-shore basin groundwater. This normalization is distinct from both NASC and NPDW in Ce/Ce* behavior, and especially in MREE behavior. The HREEs are similar to the existing normalizations.

This normalization has the benefit of removing distracting effects from the data and showing truly anomalous REE behavior, rather than all behavior that is different from the ocean (NPDW) or shale (NASC). In addition the excellent constraint on the sample collection exceeds that exercised for NASC which was compiled from 40 samples some of which had an unknown origin, and at least some of which were not even from North America (Gromet et al, 1984). Because NASC is an accepted and useful standard despite these shortcomings, WBPW could be as influential since it has about the same number of samples already, and has known locations for all its samples. We expect WBPW to evolve and improve as we and others collect more samples and leverage the method development of INL.

4. WATER-ROCK RELATIONSHIPS

The 2-by-2 matrix of Figure 5 shows a conceptual model of water and rock concentrations, and the meaning of high or low REEs in each. The matrix on the right shows the possible meanings for an open system, and the left the same for a closed system. As research continues more complex models may be proposed. All data is available on EDX.

| | | Rock | | | | | |
|------------|------|--|--|--------------|------|--|---|
| | | Low | High | | | Low | High |
| Open Water | Low | Water removes REEs and is replaced with recharge water | Rocks are stable due to refractories or kinetics, water doesn't matter | Closed Water | Low | Rocks always had low REEs | Rocks are stable in the water's chemistry |
| | High | Rocks are unstable, the water is flushing but remains in equilibrium | Water carried in REEs from elsewhere and cannot carry more | | High | Rocks are unstable, equilibrium is far to the water side | Rocks always had high REEs |

Figure 5: These 2-by-2 matrixes show the possible explanations for all combinations of Low and High REE water and rock signatures. Discovering whether the system is open or closed alters the interpretation. Hydrologic gradients and petrographic “flushing” indicators could signal which matrix is appropriate. The exposure and weathering of the Bear Lodge Carbonatites is a candidate for causing the high water and rock REE conditions found in the far right, lower box.

4.1 Rock sample REE interpretation

Rock samples were collected to best represent intervals and formations where water data was collected. Samples were evaluated for REE concentration and plotted on UCC and NASC normalized spider diagrams. Comparison of all rock samples to each other was accomplished by all samples being NASC normalized. Four primary REE patterns are recognized; (1) Primary igneous REE patterns (LREE-enriched, Eu-negative anomaly, and reduced HREE concentrations), and clastic sediment (sands and siltstones) patterns reflective of detrital source compositions from locations along basin margins, with REE profiles reflecting igneous REE-bearing host minerals. (2) clay (cation exchange Si-Al sheets) influenced patterns that are seen as MREE enrichments on NASC normalized plots. (3) organic material influenced

HREE-enriched patterns. And (4) carbonate systems which have overall lower REE concentrations than all other sediments and exhibit a flat pattern across all REE species. In some cases NASC normalized patterns for a single sample represent more than a one REE pattern type. For example, a shale sample can exhibit both MREE- to HREE-enrichment from clay abundance and still exhibit a relative LREE-enrichment reflecting continental sediment origin. It is also possible for a sandstone to exhibit a steeper than normal trend from LREE relative enrichment to lesser HREE concentrations. This type of anomaly is indicative of a greater than average REE-bearing mineral concentration, like monazite, being present within the sediment. All of these REE pattern types contribute to the understanding of primary REE concentrating species within the various rock types occurring in Wyoming basins, which in turn influence potential REE contribution into basin waters.

4.2 Water sample interpretation

Because Wyoming basins are recharged from their margins with nearly ion-free meteoric water, the WBPW normalization shows what REE patterns result from rocks interacting with pure water. (Debruyne et al., 2016), The water samples have many features seen in the WBPW normalization, which post-normalization are visible as flat areas. However, some have unique features such as the HREE enrichment in our carbonates and some carbonaceous shales. Figures 6a through 6f show the features that become visible after normalization to WBPW.

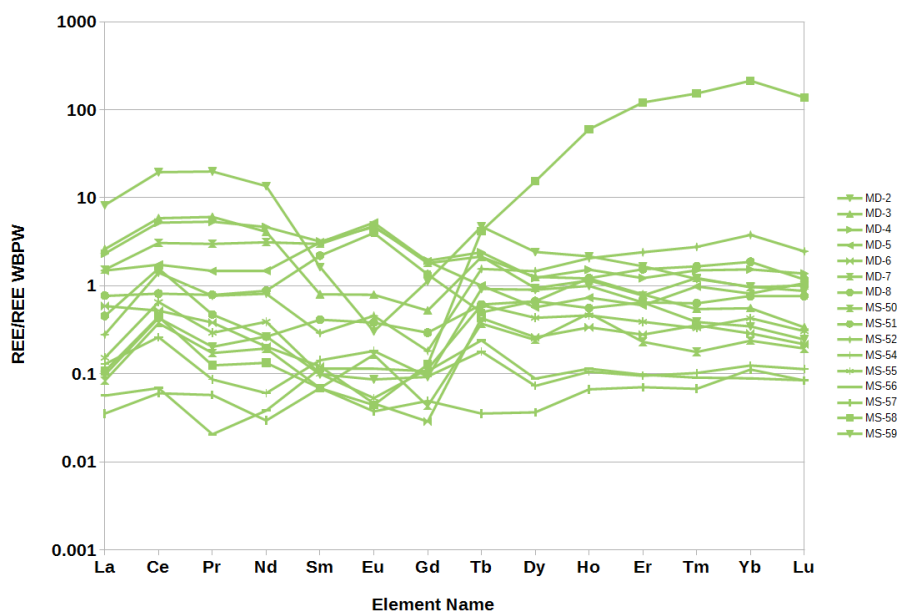


Figure 6a: Wind River Basin samples from the Fort Union (2-7, 51, 52, 57); Lance (8, 53, 54, 56); Mesa-Verde (50); and Cody (58, 59) formations. With the exception of MS-58 there is a general enrichment in LREE over HREE. This style matches the expected clastic rock system with some heterogeneity. MS-58 has HREE enrichment suggesting a fluid history that has interaction with a HREE source that readily contributes HREEs at the high temperatures found at depth in the Cody formation.

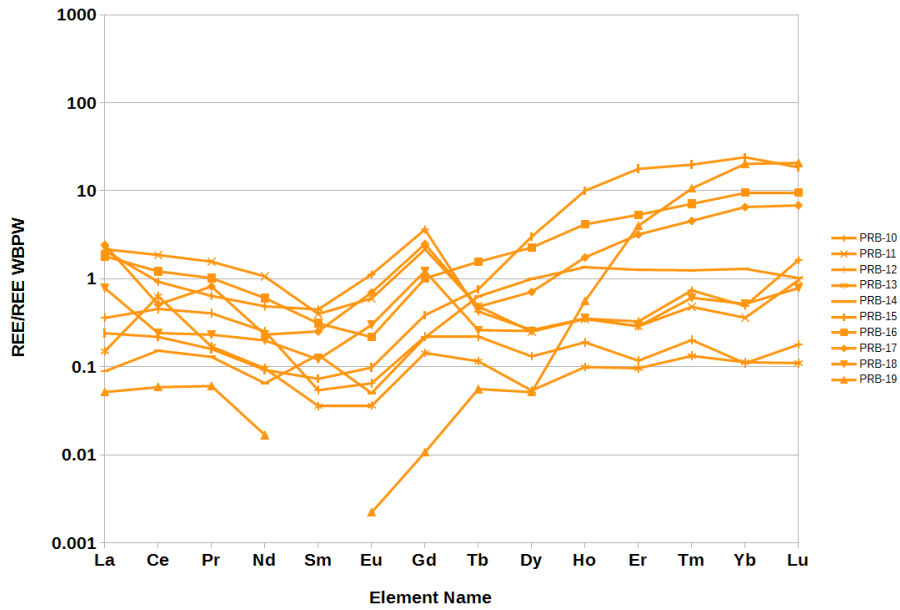


Figure 6b: Powder River Basin samples from the Parkman (12, 14), Shannon (17), Niobrara (10, 16), Turner (11, 13), Frontier (18, 19) and Mowry (15). The patterns are generally flat, but four samples (15, 16, 17, and 19) have HREE over LREE enrichments. In comparison to the other samples, which were collected from the east limb of the basin, the four HREE enriched ones are from the basin axis and contain a significant marine shale fraction in their host reservoirs. This suggests that they have picked up HREEs because the water reaching them has had a longer residence time. The other feature of all samples is the steady MREE enrichment of Gd over Eu which is not found in any other basin.

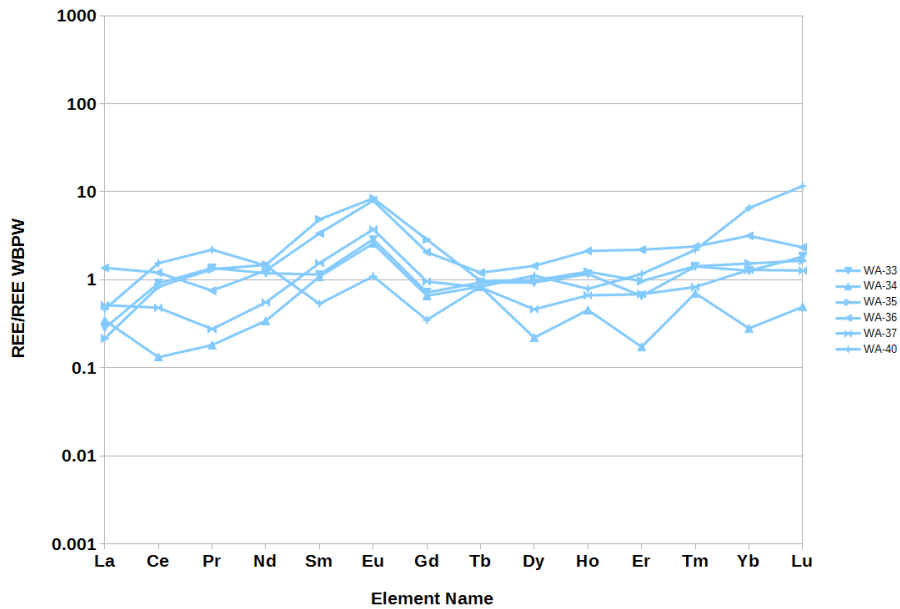


Figure 6c: Wamsutter area samples from the Lewis-Almond reservoir (all). The single-host reservoir of all these samples is reflected in their similar REE patterns. The strong Europium peak and shoulder enrichments in Sm and Gd is normally interpreted as inherited from calcic minerals, most notably Ca-feldspars and calcite. However, this is at odds with the rock data which is low in calcium. Our favored interpretation explains this behavior through the reducing reservoir conditions which are apparent in the water's ORP, and rock's vanadium enrichment. Under these conditions Eu would reduce from 3+ to 2+ and become incompatible with the minerals that formerly contained it (Sverjensky, 1984). That europium may now be responsible for the observed Eu enrichment.

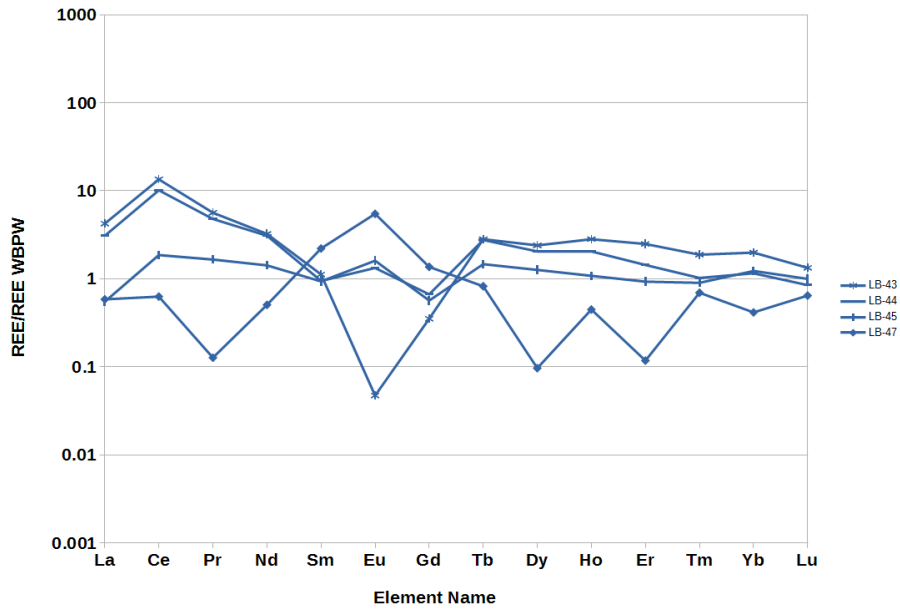


Figure 6d: LaBarge samples from the Frontier-Baxter (43, 45, 47) and Muddy (44). All LaBarge samples were collected from holding tanks and exhibit very poor conformance to the reservoir rocks. This is most likely due to differential oxidation causing some REEs to fall out of solution. The iron in the tanks is another possible culprit via a natural analog of Shannon and Wood (2005)'s ferric iron REE co-precipitation method.

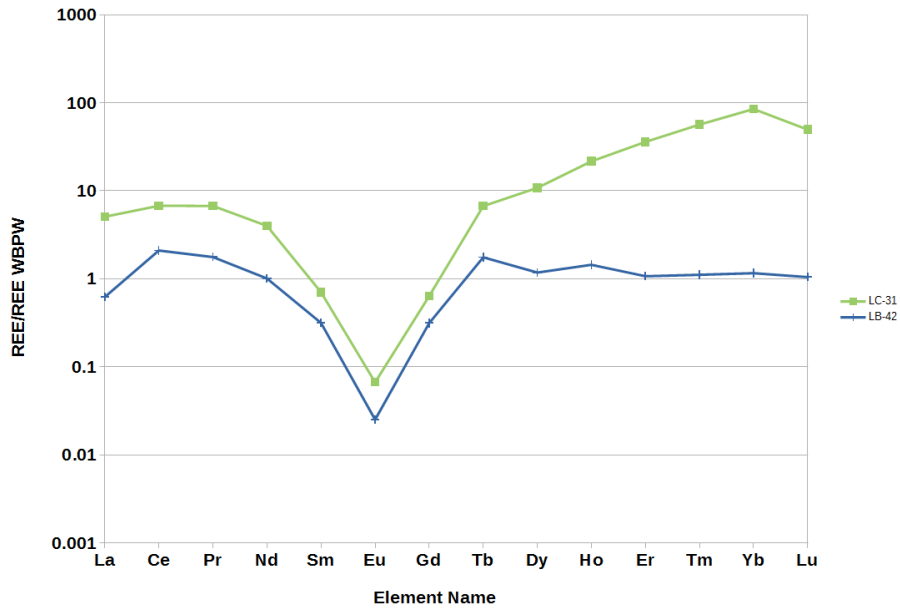


Figure 6e: The samples from the Madison in the Green River Basin (42) and the Wind River Basin (31) are very similar. They share a significant europium negative anomaly. The low Eu anomaly shows that what little Eu is present in the Madison, remains in the rock. The HREE enrichment in the Wind River Basin could be caused by hydrothermal alteration observed in basement just below the Madison.

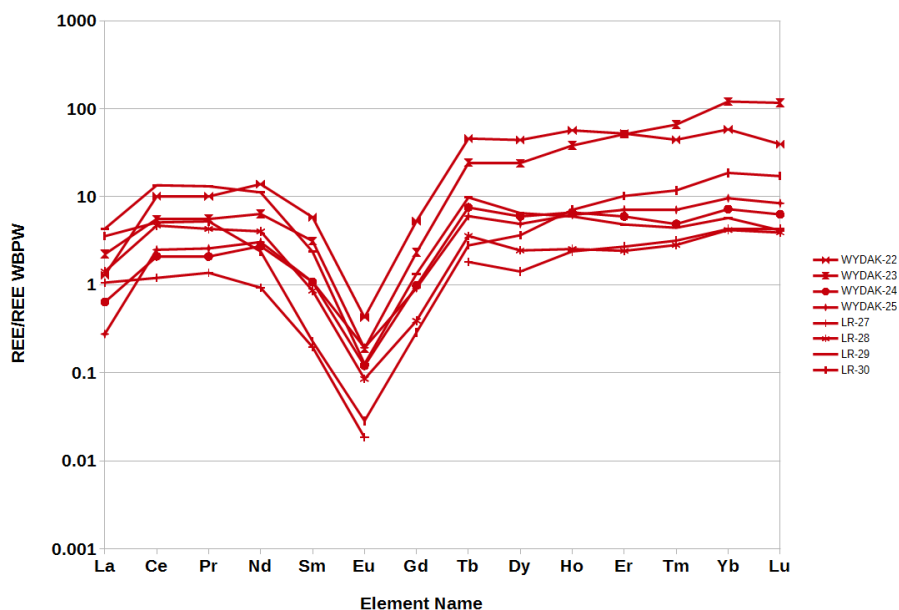


Figure 6f: Industrial power stations control their SO_x and NO_x emissions with a lime slurry used in their flu-gas scrubbers. The similarity of these power station waters, which come from contact with that slurry and the Maddison in Figure 6e suggests that even in an oxidizing system carbonates don't have significant Eu to contribute to water.

5. CONCLUSIONS

When REEs were first shown to be mobile the leading hypothesis was that they inherited the REE signature of rocks in a proportional relationship. While our findings support this sometimes, it is not always true because the signatures are imperfect matches. There must be a process or group of processes that cause REE fractionation during the transmission of REEs from rocks to water. This fractionation may be based on fluid history and host rock interaction, ligands associated with water-rock system over its entire history from basin margin to deep basin axis (Migdisov et al., 2016), and/or valence state preferences of REEs in different geologic settings (i.e. surface meteoric waters stripping feldspars and host minerals vs reduced deep basin waters involved with carbonates, diagenetic species (clays, feldspars, etc), and very long fluid histories.

5.1 Current understanding

REEs are significant in water, and do not imitate the NASC. They vary greatly over small distances, with some samples less than a mile apart containing orders of magnitude more REEs. The current interest in critical materials (Chu, 2011) such as HREEs and Eu should consider aqueous sources as our works has shown that aqueous solutions contain these in the greatest abundance, and in a form that is more easily extracted than hard-rock deposits.

When fractionation occurs as rock contributes REEs to water, it follows three modes: HREE enrichment, MREE enrichment, and MREE depletion.

The HREE enrichment mode is associated with high temperatures, and possibly sour-gas. The high-temperatures are a necessary though not sufficient requirement for this mode HREE enrichment, and are generally still over 40°C at the time of collection. Due to cooling in the wellbore, and residence time in the separator, this temperature upon collection certainly indicates a hotter environment in the reservoir, most likely in excess of 80°C. This conclusion finds support from the industrial power station analogs of natural waters, where heat from combustion encounters water and pulverized rock in either the fly-ash scrubber or the bottom ash transport pipeline. While Wyoming coal burned for this purpose is famous for its low sulfur content, it nevertheless contains significant concentrations that may support the importance of sulfur species to this fractionation mode.

The MREE enrichment mode is less speculative than the other modes. The two valence states of europium are well established as responsible for anomalies in rock investigations because reduction can make europium incompatible with sites the other 3+ REEs could fit, or oxidation could make europium incompatible with 2+ substitution sites such as the well-established calcium substitution in carbonates and calcites. This mode appears to contribute some Gd and Sm in addition to the Eu, as a Eu anomaly is always parroted by these two neighbor REEs. While both Gd and Sm can have redox states other than 3+ (including 2+) they almost never adopt those states in nature, leaving this detail of MREE behavior something of a mystery.

The MREE depletion mode is seen only under two conditions. The first is calcium-bearing rocks which may not have significant REEs to begin with (Figure 5, right, top-left box). The second is samples collected from steel tanks, where iron oxide may scavenge the Eu from solution, as seen in Figure 6d.

5.2 Future investigations

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 strong reducing agent, and 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.

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 those states show the same Gd signature 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.

5.3 Funding sources, acknowledgements, and conflicts of interest

Funding for this work was provided by DOE EERE - Geothermal Technologies Program award number DE-EE0007603. The authors would like to thank our industry collaborators for site access and permission to sample. This work benefited from the efforts of Yuriy GANSHIN who performed the calculations for the normalization, and produced Figure 2; Travis MCLING and Ghanashyam NEUPANE who performed the REE extractions and ICP-MS analysis; and Fred MCLAUGHLIN who performed optical petrographic analysis of the rock samples. The authors declare no conflict of interest.

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