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Applying the Wyoming Basin Produced Waters Normalization Alongside NASC: How REE Anomalies in Matched Geothermal Water and Rock Datasets Yield More Than the Sum of the Parts

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ABSTRACT

The United States generated an estimated 890 billion gallons of produced water during oil and gas operations in the 2012 calendar year (Veil, 2015). Produced water is typically saline, contains dissolved materials of value, and is of elevated temperature. In this work we examine a subset of the water and rock data generated by University of Wyoming, Idaho National Labs, and U.S. Geological Survey under their project DE-EE0007603. The water data we consider describes REE concentration and geochemistry of produced water in the Wind River Basin and the Powder River Basin of Wyoming. The rock data we consider describes the REE concentration and whole-rock geochemical data of the reservoir host rocks. We apply the Wyoming Basin Produced Waters (WBPW, Nye et al., 2018) and North American Shale Composite (NASC, Gromet et al., 1984) to identify significant features in these waters and rocks in a combined approach.

Two case-studies show the benefits of this combined water and rock approach. In the first, gadolinium (Gd) and HREE anomalies in the Powder River Basin can be explained by Cannonball Sea influence, and basin margin recharge, respectively. In the second, europium (Eu) and HREE anomalies in one of the deepest (>7,600m) wells in Wyoming can be explained by hydro-geothermal leaching from the basement granite, and subsequent loss of LREEs during water migration to shallower reservoirs. In these case studies, the combined water and rock approach not only improves description of the system, but also independently predicts a local phenomena that had been previously proposed by Nealson et al., (2009).

The combined water and rock approach allows more robust conclusions than in the original work of Nye et al. (2017). The approach recognizes that reactions with the reservoir rocks appear to be the primary factor in aqueous REE behavior.

1. INTRODUCTION

REEs have enabled identification of chemical reactions that cause fractionation among the REEs, and tracing physical movement of water and rock with unique signatures. Historically REEs in rocks have been used to divine the composition of earth's mantle and whole-crust (e.g. Gast 1960, Haskin et al. 1966, Taylor 1964), identify the crystallization events that occurred as a magma cooled (Hanson 1980, Condie 1993), and estimate how much sediment was contributed to basin fill by each possible mountain range on that basin's margin (Qiu, 2015). Analytical improvements allowed measurement of REEs in water opening new ways to study the ocean's oxic/anoxic zonation (DeBaar, 1985), geothermal groundwaters' flow paths (Nelson, 2005), the changes in the world's oceans as they flow around the continents (Byrne and Sholkovitz 1996), and even the provenance of wine (Piper and Bau, 2013).

Almost all applications of the REEs leverage their nearly identical behavior in nearly all situations. All lanthanide REEs have smoothly decreasing covalent radii from 207pm (La) to 187pm (Lu), a consistency which is not seen elsewhere in the periodic table (Wolfram, 2018). The electronegativity of all REEs is similarly consistent, ranging between 1.1 and 1.27. Oxidation states are of special significance in the earth system, and the REEs are almost always found in $^{3+}$ oxidation states in nature, although Eu^{3+} and Ce^{3+} can occur as Eu^{2+} and Ce^{4+}. These similar chemical traits result in REEs responding to most natural situations in nearly the same way.

An example of this near similar behavior is in the crystallization of allanite and zircon in the last stages of a granodiorite pluton cooling from magma. Although the lattice of each mineral can accommodate each of the REEs, the allanite lattice more readily incorporates Light REEs (LREEs), and the zircon lattice more readily incorporates Heavy REEs (HREEs) (McLennan, 1989). This fractionation can then be maintained in subsequent physical weathering and amplified if sorting during transport separates allanite and zircon grains into different geographic locations.

Although fractionations like the above example are well established in past studies of rock REEs -- and to a lesser extent past studies of water REEs -- to our knowledge no work has attempted to identify fractionations inherent to the dissolution of REEs. In this work, we propose that the difference between the North American Shale Composite (NASC) and Wyoming Basin Produced Waters (WBPW) normalizations could be the first step towards quantifying the natural fractionation of REEs when rock is exposed to large quantities of continental subsurface water in nature. We then present two case studies where perturbation of that fractionation suggests: 1) scouring of HREEs from a basin's margin and transport of those HREEs into the deep basin, and 2) fluid flow in geothermal conditions, which transported HREEs into a shallower unit through isolated flow paths.

2. METHODS AND DATA PROCESSING

The samples in this work are a subset of those collected for U.S. Department of Energy award DE-EE0007603. That project was studying the rare earth element concentrations of produced waters and concluded in July 2018. The present work has revisited the data produced, improved its quality, and made new discoveries. Below we provide the background of these samples in the context of their original intended use.

2.1 Sample Collection

The rock and water samples were collected between October 2015 and February 2017 in Wyoming and at the USGS Core Research Center in Denver, Colorado.

2.1.1 Water sample collection

In the Powder River Basin (PRB) samples came from sampling valves just after the on-pad phase-separator. This is as close to the well head as possible given the pressurization of the confined reservoirs in this basin. The Wind River Basin (WRB) Madison sample came from a sample valve just after a flash tank, which reduces the water to safe pressures and temperatures. The Cody sample came from a post-separator, on-pad, large holding tank.

All water samples were collected in low density polyethylene (LDPE) bottles. The 500ml bottles had been HCl acid-washed and rinsed with ultra-pure water (>18 MΩ-cm). The bottles were rinsed again in the field with the sample before final collection.

The water samples were transported for less than 8 hours in a cooler with dry ice. The samples were frozen overnight to arrest biological activity. The following morning, they were thawed, filtered, split, and acidified. Filtering used 0.45 micron MCE 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 this 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.

2.1.2 Rock sample collection

Samples were collected at the USGS core library in Denver, Colorado. Individual cores were selected for review based on formation type and proximity to produced waters samples of this investigation. Variability in individual cores was assessed during core plug selection based on mineralogy, diagenetic character (including cementation and alterations), and overall sedimentology of the cores. Representative intervals, those with the most promising fluid accommodation (porosity and permeability) were selected in addition to bounding layers of aquifer systems relating to produced water samples. Every effort was made to select a suite of samples representing the aquifer rock of each water sample.

Core plugs were removed from the selected core by USGS specialists and bagged for use in this investigation. Plugs were then divided into segments based on analysis needs including thin sections, geochemistry evaluations, cation exchange experiments, XRD analysis, and SEM analysis. If enough sample remained it was stored for future use.

2.2 Sample Analysis

As part of the same Department of Energy project, water and rock were sent for analysis at internal and external laboratories.

2.2.1 Water analysis

Measurement of pH, temperature, conductivity, and Oxidation-Reduction Potential (ORP) were taken in the field with a hand-held Myron Ultrameter II. Monoatomic and polyatomic anions were analyzed by Ion Chromatography at Energy Laboratories. Cations were analyzed as elements by ICP-OES at Energy Laboratories. Aqueous REEs were analyzed by ICP-MS after resin cleaning and pre-concentration under the methods of (McLing et al., 2014) at Idaho National Laboratories.

All data resulting from these analyses are in the DE-EE0007603 final report (Quillinan et al., 2019). Those data are available on the Geothermal Data Repository: https://gdr.openei.org/submissions/1125.

2.2.2 Rock analysis

All samples were initially analyzed for major, minor, and trace elements, per standard procedure for geochemical evaluation. This external analysis was performed by ALS Geochemistry (Reno, NV). Representative thin sections for every sampled plug were made by Wagner Petrographic (Lindon, UT) and analyzed in house at CMI, using a Zeiss Axio A1 transmitted light microscope.

Based on initial geochemical and element characterization of major, minor, and trace components, individual samples were identified for additional evaluation by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) methods (conducted at both the University of Wyoming and Idaho National Laboratory-Center for Advanced Energy Studies). XRD methods were used to identify mineral species. Determination of mineralogy, element speciation, concentration, and elements fractionation from hydrothermal alteration was the focus of SEM investigations. Area spectral mapping, point spectra, and general physical character of samples were determined with SEM methods. These data are available in the same report as above, and the granitic basement samples described in http://gdr.openei.org/submissions/926.

2.3 Interpretation of Anomalous Lows and Highs in REE Concentrations

The WBPW as described by Nye et al. (2018) records the average REE concentration of 38 produced water waters from Wyoming. The WBPW shows a roughly 6 order of magnitude difference between REE concentrations in typical continental groundwater, and typical sedimentary rock (NASC) as described by Gromet et al. (1984). Figure 1 shows the comparison of these two normalizations. Two conclusions from the comparison are 1) that a typical continental water acquires only about a millionth of the REEs in a typical continental rock, and 2) that those REEs which the water acquires from the rock fractionate during equilibration.

WBPW has some anomalous elements which behave differently from their neighbors and also an overall enrichment of high atomic number REEs (HREEs) over low atomic numbers REEs (LREEs). Cerium in WBPW is lower than one would expect based on its neighbors and its behavior in rocks, possibly due to oxidation of Ce(III) to less soluble Ce(IV), which mirrors cerium's behavior in the ocean. Samarium is elevated inexplicably, especially considering that its concentration by mass is normally much less than its lighter neighbor, neodymium. Europium is significantly elevated, to the point of being the most concentrated REE in continental basin waters, likely due to its oxidation from Eu(II) (which substitutes for calcium in many minerals) to Eu(III) (which cannot occupy the same parts of the crystal structure) causing a surplus of available europium for aqueous transport. Gadolinium is also significantly elevated in waters, possibly through the same electron shell behavior that causes gadolinium's enrichment in the ocean (Alibo and Nozaki, 1999).

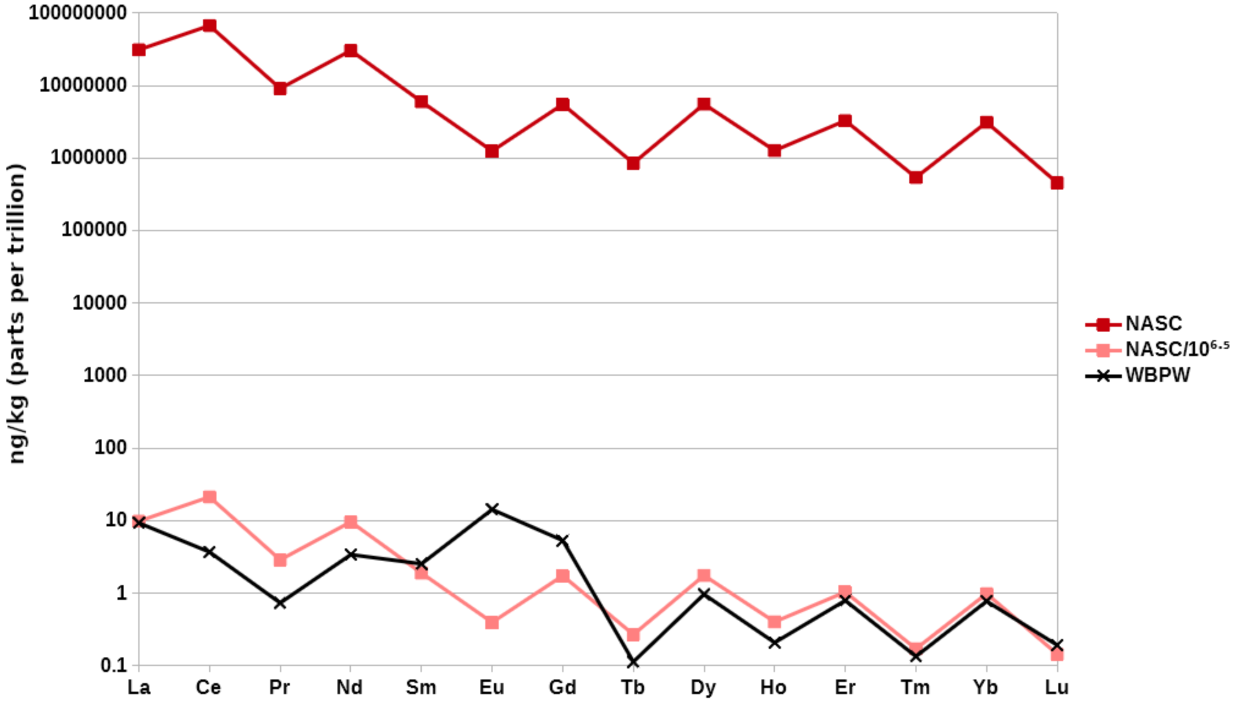


Figure 1: The WBPW is 6.5 orders of magnitude more dilute than the NASC. Shifting the NASC down by that increment (pink line) makes the structural differences more visible. These structural differences include four elements (Ce, Sm, Eu, and Gd) behaving differently from their neighbors and the conforming elements showing a higher HREE-LREE ratio.

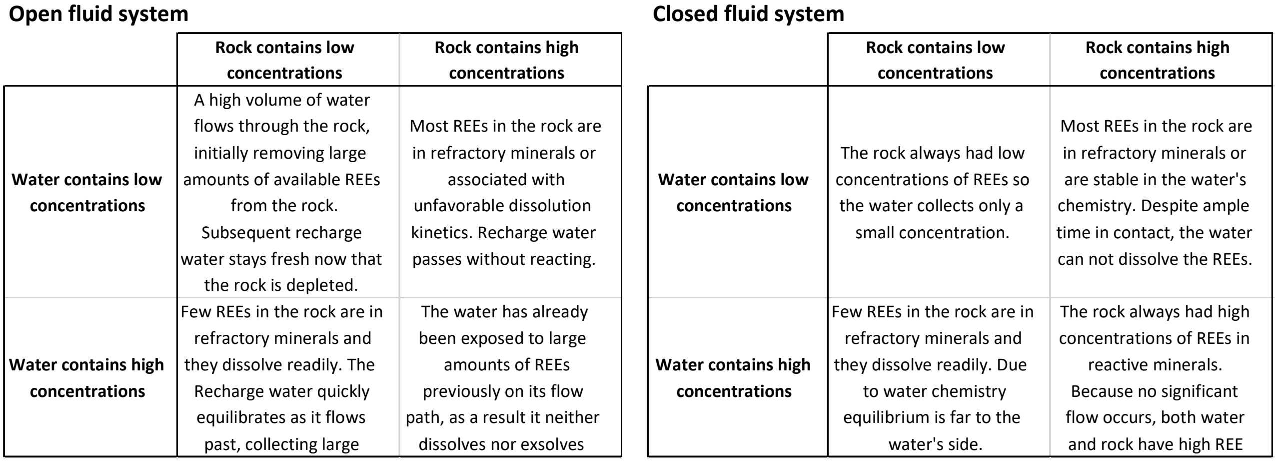
In the following two case studies we show that assessing a produced water's deviations from WBPW, and assessing a rock's deviations from NASC can result in an improved interpretation because the structure of these two normalizations is different. The 6.5 orders of magnitude between waters and rocks is important to keep in mind because a trivial change for rock is often significant in water. This difference in reservoir concentrations suggests direct comparison of water and rock would be unfruitful. However, comparison of a water to WBPW is possible, as is comparison of a rock to NASC. The resulting assessment of anomalous lows and highs can suggest that a water lost REEs to rock or a rock lost REEs to water, even if the change is not significant enough to show up in the other phase.

3. OPEN AND CLOSED REE SYSTEMS

A comparison of waters to WBPW showed that some waters had more REE than expected, and others less. Similarly, when rocks were compared to NASC, some of them had less REE than expected. We split the samples into two groups depending on whether they had lower or higher REEs than the normalization. If a sample mostly conformed to the typical behavior in a normalization, but had a HREE or LREE deviation, it was grouped by whether that deviation was high or low. We then matched the low and high anomalies to possible causes. This matching showed that the ability or inability of water to leave the system, such as by basin flushing at the end of the last ice age, was key to understanding the process that occurred.

3.1 Data grouping suggests a 2x2 matrix

The 2-by-2 matrix of Figure 2 shows a conceptual model of water and rock concentrations, and the interpretation of what high or low REEs mean in each case. 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. The data we studied to generate these matrices is available on EDX and the GDR (Quillinan et al., 2019).



Open fluid system

	Rock contains low concentrations	Rock contains high concentrations
Water contains low concentrations	A high volume of water flows through the rock, initially removing large amounts of available REEs from the rock. Subsequent recharge water stays fresh now that the rock is depleted.	Most REEs in the rock are in refractory minerals or associated with unfavorable dissolution kinetics. Recharge water passes without reacting.
Water contains high concentrations	Few REEs in the rock are in refractory minerals and they dissolve readily. The Recharge water quickly equilibrates as it flows past, collecting large	The water has already been exposed to large amounts of REEs previously on its flow path, as a result it neither dissolves nor exsolves

Closed fluid system

	Rock contains low concentrations	Rock contains high concentrations
Water contains low concentrations	The rock always had low concentrations of REEs so the water collects only a small concentration.	Most REEs in the rock are in refractory minerals or are stable in the water's chemistry. Despite ample time in contact, the water can not dissolve the REEs.
Water contains high concentrations	Few REEs in the rock are in refractory minerals and they dissolve readily. Due to water chemistry equilibrium is far to the water's side.	The rock always had high concentrations of REEs in reactive minerals. Because no significant flow occurs, both water and rock have high REE

Figure 2: 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. Conversely, an open or closed system can be inferred if the indicated explanation for one is plausible and the other implausible.

3.2 Categorization of the data

The two groups of rocks considered in this paper are: the PRB Cretaceous sedimentary units (Figures 3 and 4), and the WRB Madison Limestone (Figure 4). For readability, the PRB is split into shales and sandstones. These patterns are mostly the same, except as noted in the caption. The most significant difference is that the Madison Limestone is one order of magnitude lower concentration in all REEs. Accordingly the PRB cretaceous sedimentary units were classified as slightly low and the Madison Limestone as low.

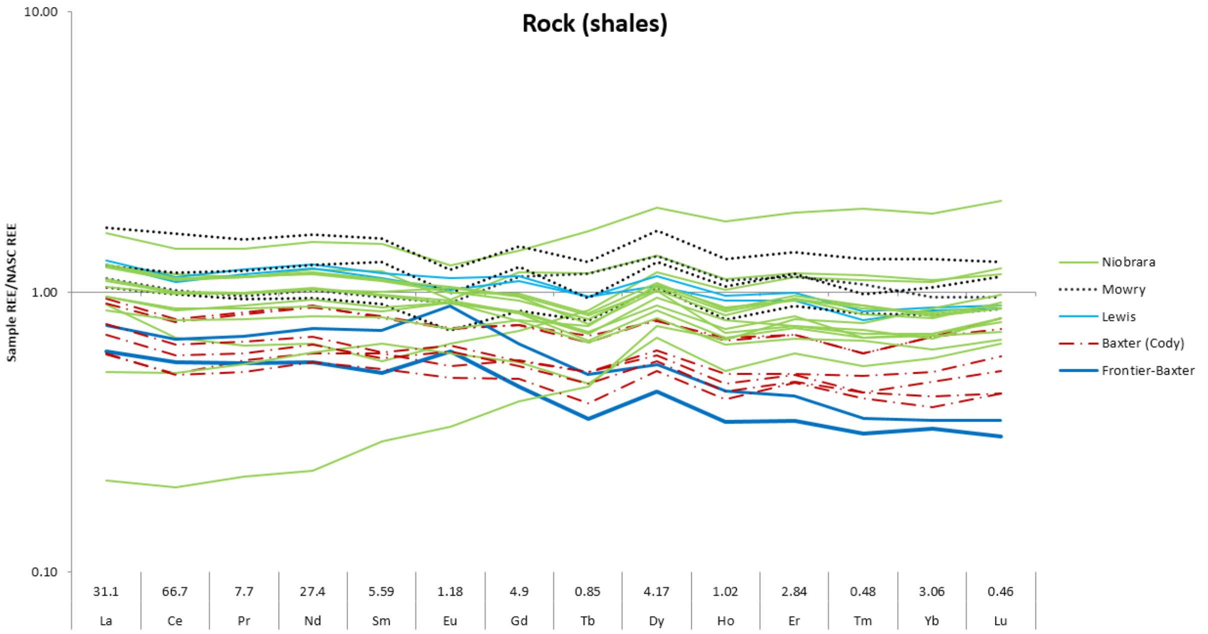


Figure 3: Excepting some anomalous LREE depletion and HREE enrichment in the Niobrara, and negative europium anomalies in the Mowry formation, the sedimentary rocks of the Powder River Basin conform to typical NASC composition. If there is a general deviation from NASC, it is a small HREE depletion.

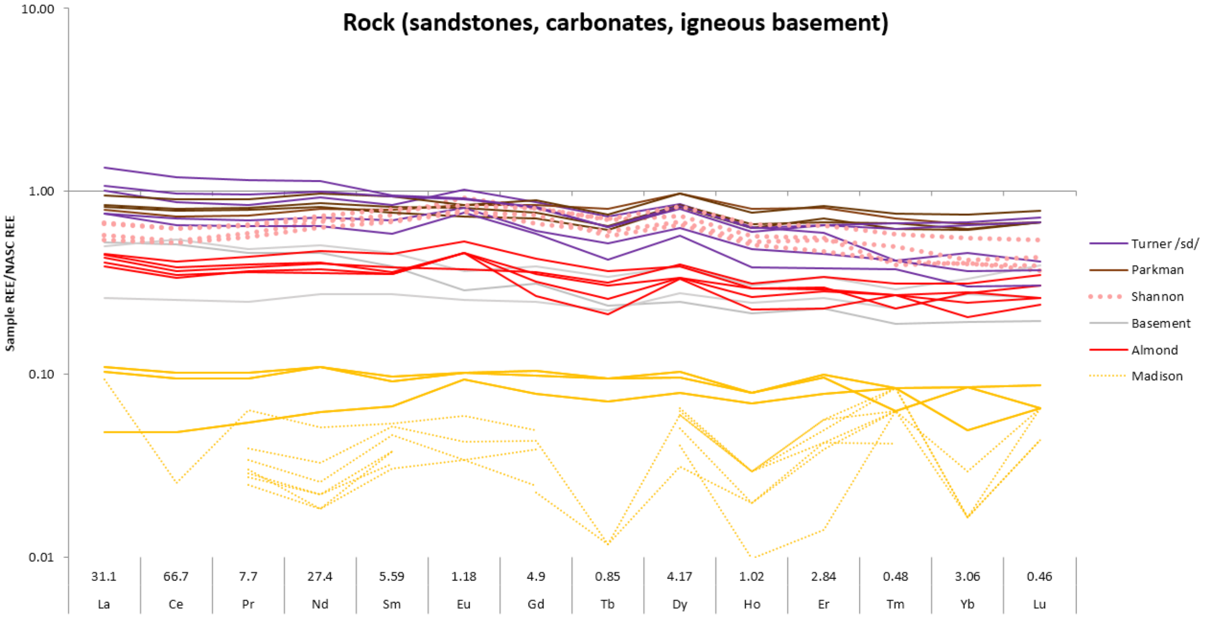


Figure 4: The sandstones of the PRB have similar REE behavior to the shales of that basin. The concentration of REEs in the Madison Limestone is significantly less, to the point that some REEs were outside the range REE rock analyses are normally calibrated. These samples (dashed yellow lines) do not have meaningful structure but do indicate that the Madison Limestone has very low REE concentrations.

The two groups of waters considered in this study are from the Cretaceous sedimentary units of the PRB (Figure 5) and the WRB's Madison Limestone and Cody Formations (Figure 7).

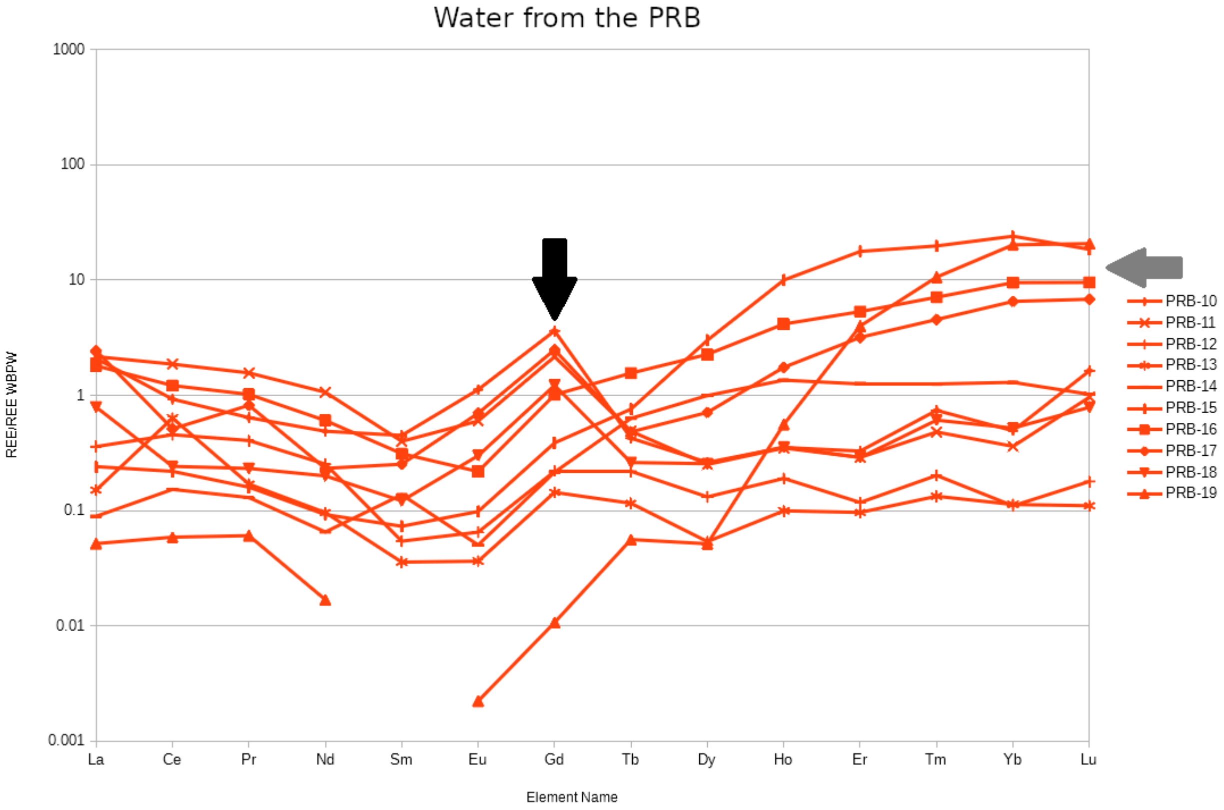


Figure 5: Shows the concentration of REEs in Powder River Basin samples. All water samples shown here are from the Cretaceous petroleum system. The petroleum in that system is self-sourced or migrated in from lower units (Anna, 2010). Because these samples are contemporaneous with the Western Interior Seaway, a flushing or inundation event is a probable means to introduce the Gd anomaly (black arrow). Only in the center of the PRB do HREEs show some enrichment (grey arrow). This suggests rapid uptake of Gd in the basin margin recharge zone, and slower uptake of HREE only after sufficient time, temperature, and depth.

4. CASE STUDY: GD AND HREES IN MARINE-INFLUENCED UNITS OF THE POWDER RIVER BASIN

The Cannonball Arm of the Western Interior Seaway covered the PRB at the Cretaceous-Paleocene boundary (Blakey 2014) and likely introduced a unique REE signature to the recently deposited Cretaceous units. We interpret these rocks to have always been slightly low in REE content. However, we show HREE and Gd features in the aqueous REEs which suggest that 1) open-system flushing is occurring in the basin, and 2) the Cretaceous marine influence is still reflected in the water analyses.

4.1 Gadolinium Features in the PRB

One way for gadolinium to be introduced to a sedimentary rock system is through interaction with seawater. A positive gadolinium anomaly is present in seawater regardless of how it is normalized (DeBaar et al. 1985, Alibo and Nozaki 1999). This anomaly is most likely caused indirectly by the configuration of its electron shell ([Xe]6s24f75d1) which results from the similarity of the total pairing energy and the difference in energy between the 4f and 5d orbitals. This electron configuration gives gadolinium the greatest multiplicity under Hund's Rule (Hund,1925), as well as an anomalously large ionic radius, ionization energy, and pure-element ferromagnetism near room temperature (Wolfram, 2018). One or more of these traits might be responsible for gadolinium's greater than predicted presence in the ocean.

REE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ng/kg	5.38	0.56	0.72	3.43	0.68	0.19	1.07	0.18	1.36	0.39	1.33	0.21	1.45	0.26

Figure 6: The elemental concentrations reported by Nozaki (2001) for North Pacific Deep Water (NPDW) converted to ng/kg. In addition to the gadolinium positive anomaly, ocean water has a cerium negative anomaly.

The Western Interior Seaway and Cannonball Arm covered the majority of the Powder River Basin for almost all of the Cretaceous Period and Paleocene Epoch respectively. Thus, seawater influence persisted particularly long in the Northeast corner of Wyoming, and produced a positive gadolinium anomaly greater than found in other Wyoming basins. Nye et al., (2018) considered that this unique distinction was indicative of the marine influence or the marine origin of the sediments contributed by Cannonball Sea arm. That work suggested that Cetaceous to Paleocene marine shales in South Dakota or maybe even the entire area associated with the Western Interior Seaway could be responsible for the gadolinium peak.

Gadolinium's anomalously high concentration in the ancestral ocean appears to have influenced Cretaceous rocks and subsequent basin waters of the Powder River Basin as shown in Figure 5, both of which exhibit a positive gadolinium anomaly. The influence of the Western Interior Seaway, specifically the Cannonball Arm, could be achieved through authigenic water trapping during deposition and diagenesis of Cannonball Sea sediments, and/or by temporary immobilization of REEs as a cement, grain coating, or adsorbed ion within these same sediments. The concentration of gadolinium preserved by this mechanism is minor enough to be absent in the pre-Paleocene rock REE record. These older basin rocks serve only as holding reservoirs for the Gd-enriched waters derived from Cannonball Sea influenced basin margins. Concentrations of Gd derived from flushing of Paleocene sediments along PRB basin margins are however high enough to contribute to the PRB's distinctive present-day signature within the waters sampled to date.

The observed gadolinium anomaly is present in all water samples from the PRB, suggesting that Gd is mobile in the aqueous phase, but that it is not so mobile as to be entirely swept from the basin margins by modern rainwater recharge. Gd may also be retained in the sediments sourcing gadolinium because the six order of magnitude difference between water and rock allows contribution of gadolinium at a concentration that is significant to water, but insignificant to the host sediments. The sediments hosting the anomalous gadolinium tend to be low porosity and low permeability rocks which result in low fluid transport rates and likely long time periods to move REEs into fluids completely. Gadolinium behavior suggests that the PRB is an open-system, but that the rock phase can contribute high Gd without itself being significantly depleted.

The gadolinium anomaly has traits that confirm it is not an analytical artifact. First, most gadolinium positive anomalies in Quillinan et. al. (2019) are small "rider" peaks on the side of a much larger europium peak. However, in the PRB gadolinium surpasses the concentration of europium both after and before normalization. Second, the other gadolinium anomalies in Quillinan et al. (2019) are symmetric with the samarium rider peak on the other side of europium. Accordingly, evidence of anomalous gadolinium behavior comes from comparing it to samarium, which instead of being approximately equal, is surpassed by gadolinium. This means the gadolinium anomaly in the PRB is too significant to be an interpretation artifact and must be an actual anomaly in nature.

4.2 HREE Features in the PRB

HREEs are elevated in four PRB samples from the middle of the basin. The other samples from the PRB have more typical HREE concentrations and are from nearer the edge of the basin. While all of the HREE-elevated samples have similarly high erbium through lutetium, their HREE enrichment starts more or less suddenly between terbium and holmium. This difference between basin center and the samples from the syncline's limb suggest that HREEs enter the water, but not immediately.

Because recharge in the PRB mostly comes from the basin margin, the water samples low in HREE have had less time to react with the reservoir rock. The samples come from a variety of formations which suggests that formation is not a control on this reaction, and further that every formation sampled contains the necessary minerals to contribute HREEs to water. The control on whether HREEs are accumulated or not seems to vary only by the well's position on the flow path. This relationship between HREE concentration and flow path position limits factors allowing delayed uptake of HREEs to temperature, which increases with depth, and reaction kinetics, which are time sensitive. Additional sampling at intermediate points on the flow path could assist in determining which factor is controlling HREE accumulation in the water.

There are two aqueous REE features in the PRB, a HREE enrichment and gadolinium enrichment. Neither one of these enrichments appears to affect the rocks of the PRB enough to be identifiable in those rock's REE behavior. Both of these enrichments are confined to the fluid phase of the system. This indicates the PRB is an open system with available Gd and HREE. The Gd is rapidly accumulated into the water on the basin margin and remains similarly enriched in the center of the basin. The HREEs are accumulated more slowly, and only attain significant enrichment in the center of the basin.

5. CASE STUDY: HREE AND EU IN THE WIND RIVER BASIN

The Wind River Basin contains Cretaceous sedimentary units like those found in the PRB. Those units lack the gadolinium anomaly described above, likely because the Cannonball Sea did not extended far enough west to contribute element constituents, so the marine-influence was not transferred to the water and rocks in the WRB. Additionally, the Western Interior Seaway itself was limited in extent and time in the WRB compared to the PRB. However, those shallow units have a significant positive europium anomaly, which in both basins is attributed to the oxidation of rock-compatible Eu(II) to rock-incompatible Eu(III), and the resulting aqueous uptake of the readily available excess europium.

This REE pattern in Cretaceous sediments (Figure 4) differs from the deeper, low-europium, Paleozoic units of the WRB (Figure 7). In the WRB's Madison Limestone it is difficult for europium to oxidize because hydrocarbons maintain a reducing environment and the groundwater's longer flow path transports less oxygen to such depths. Accordingly the europium is not liberated from the rock by oxidation state incompatibility. Figure 7 shows that very little europium dissolves into the Madison Limestone water, but that significant HREEs are present.

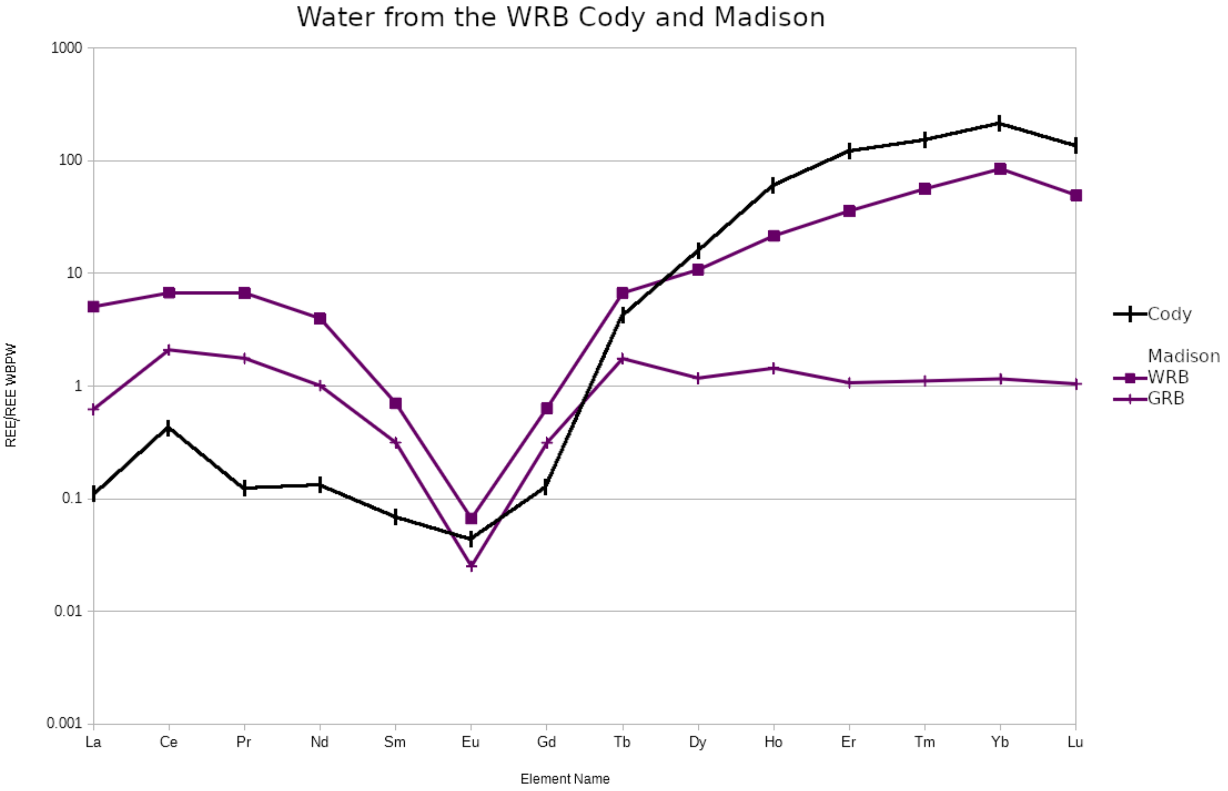


Figure 7: The waters in contact with the Madison Limestone have anomalously low europium compared to WBPW. In the WRB where the Madison Limestone sits directly on top of the granitic basement it has more HREEs than in the GRB where multiple Cambrian units insulate it from the basement. The Cody has even greater HREE concentration than the Madison.

5.1 HREE Transport: An Open Hydrogeothermal System

The Madison Limestone in the WRB unconformably overlies the granitic basement. The Madison in the WRB has HREE enrichment as seen in Figure 7 above. In contrast, the Green River Basin Madison overlies the Flathead Sandstone, Gros Ventre Formation, and Gallatin Limestone which insulate the Madison in that basin from the granitic basement. In the Green River Basin no such HREE enrichment occurs.

This contrast coupled with observed bleaching of the granites underlying the Madison (University of Wyoming, 2017) suggests that HREEs are being leached by hot, reduced, aqueous fluids out of the granitic basement and transported through the Madison to the Cody, some 8,300feet shallower. Because no similar enrichment in HREEs is found above the Cody, the flowpath either stops there, or a geochemical change such as temperature causes the majority of HREEs to be deposited in the Cody while the water continues on. The Cody HREE behavior could include a pre-existing HREE enrichment, which is seen in some other shales. Faults that cover this basement to Cody interval have been well established in maps of the Wind River Basin since Keefer (1970) (WSGS, 2015).

The low REEs seen in the Madison carbonate rocks (Figure 7) support that the model that HREEs seen in that water were neither locally sourced nor locally deposited. HREEs found in waters associated with the Madison carried their HREE load in from below, and continue to carry those HREEs through the Madison up into the Cody Shale.

A challenge to the above model is that units that trap natural gas should also trap water, and since the Madison Limestone is a significant hydrocarbon reservoir, no water should be able to escape to carry an HREE load to shallower units. Nealson et al., (2009) explained how this apparent contradiction resolves by identifying independent the gas and water flow and storage systems in WRB units below the base of the Meeteetse Formation. This explanation is especially attractive because the escape conduit that allows water to leave the Madison could terminate in the Cody and help explain the HREE enrichment of that formation. Additionally, carbonite precipitation as fracture fill or pore cementation while the water rises these 8,300 feet could account for the lower LREEs seen once the water is in the Cody Shale.

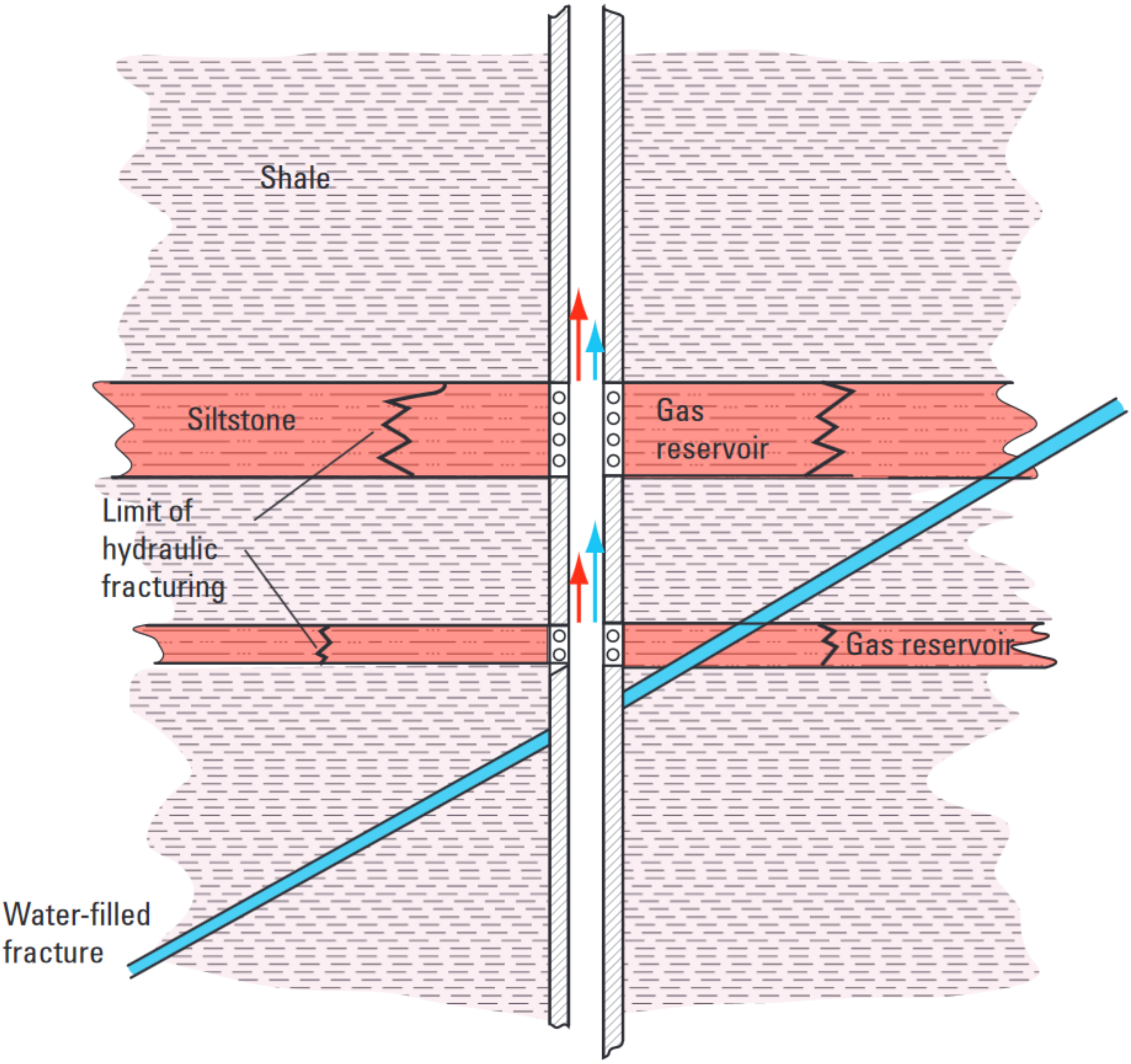


Figure 8: From Nealson 2009, A dual-permeability system was proposed to explain the timing of gas and water kicks in production data, here we support it to show water migration without gas. (Other explanations include faults contacting the Madison at a structural low, keeping buoyant gas from reaching the fault, or completion of the REE leaching process before gas migrated into the Madison).

5.2 Eu Depletion: Another Open System

Europium is normally found in geochemical systems as Eu(III). However, in highly reducing environments it can occur as Eu(II). In the igneous processes that form calcium feldspar (anorthite) Eu(II) is stable and can substitute for Ca(II) in most crystal latices. This ability to substitute into a common mineral and become incompatible upon oxidation makes europium unique among the REEs.

If arkosic sandstones encounter oxidizing conditions, that favor Eu(III), the europium no longer fits the anorthite lattice, and that instability makes it easily released. Positive europium anomalies in rocks, especially those that occur in unfractionated igneous rocks, have a surfeit of europium to contribute to groundwater after oxidation and weathering. Figure 8 Shows the pH-Eh control on europium's most stable phase in typical PRB groundwater chemistry. Although kinetics and local availability of oxidizer undoubtedly keep significant Eu(II) in the rock, the wide range of environments where Eu(II) is more favorable than Eu(III) suggest not only efficient liberation of europium, but also that Eu(III) can only be reduced back to Eu(II) near/outside the stability field of water. This means that once mobilized and oxidized to Eu(III) the europium will almost never return to Eu(II).

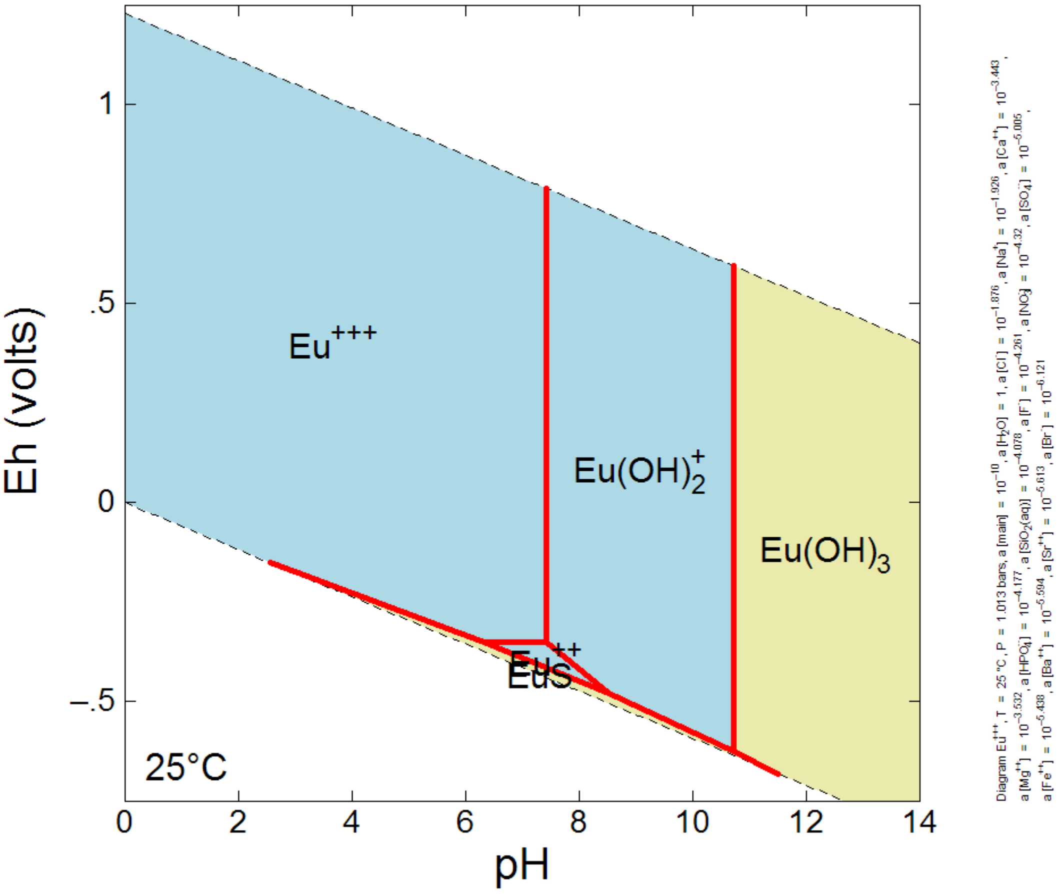


Figure 9: A typical groundwater, even with significant sulfate, can only support significant Eu(II) at a narrow range of neutral pH and extremely reducing conditions. Because these conditions are so near the stability field of water, they are unlikely to occur in nature.

Because exchange of europium from rock to water is practically one-directional, continental waters typically have a positive europium anomaly. This anomaly is so significant that europium typically makes up a greater percentage of the total aqueous REEs by mass than lanthanum (Quillinan, et al. 2019).

With appreciation for this Europium behavior, the atypical negative europium anomaly seen in the Cody and Madison waters becomes very important to understand that system. This negative europium anomaly is found in many waters that are associated with carbonate rocks (Nye et al. 2018). Carbonates, as seen in Figure 4 as yellow lines often have very low concentrations of all REEs due to the circumstances of their formation.

The interpretation we propose is that the carbonates, which had low REEs over their entire history, were only exposed to water along limited flow paths. The water in those flow paths was hot but reducing, and so liberated less europium than water normally does. In appreciation of the Madison Limestone's old age and long period of burial at depth, most of the europium that was in rock near water-filled fractures has been removed and carried away over the last 350Ma. As a result the modern water in the Madison Limestone has lower concentrations of europium because there is less in the exposed parts of the rock. The role of natural fractures limiting water-rock contact is important because whole-rock analysis of the Madison Limestone shows depletion in all REEs rather than selective loss of Europium.

In combination with the HREE anomaly described in section 5.1, the observed REE behavior in the Madison Limestone requires five things: 1) that fluids, possibly oxidizing, remove europium from along fractures in the Madison during burial, 2) that in the present day hot, reducing, water leaches HREE from the granitic basement, 3) that those HREE-rich waters pass through the Madison Limestone, possibly collecting more non-Eu REEs, via fractures that are independent of the Madison hydrocarbon system, 4) that those waters travel up 8,300feet via transmissive faults loosing LREEs to calcite precipitates, and 5) that the water stalls-out in the Cody Shale adding its HREE signature to the water in that formation, but retaining the low LREE and Eu signature it now has.

This model for REE behavior in the Wind River Basin can explain all rock observations: the slight depletion in the granitic basement (University of Wyoming, 2017), the low but un-anomalous REEs in the Madison Limestone, and the entirely typical Cody Shale. The model also explains the fluid and aqueous REE observations: water in the Madison Limestone is high in HREE but low in Eu, buoyant hydrocarbons such as methane are trapped in the Madison, and water in the Cody has a HREE enrichment but Eu deficiency just like the Madison.

6. CONCLUSION

The approach of comparing water to WBPW and rock to NASC allows researchers to identify anomalies in each, and then draw conclusions on the interaction of water and rock. The comparison can result in detection of an open system and sometimes even deduce what REEs are lost to a different formation. Here, we demonstrated that in the WRB the Madison Limestone not only started with only 10% of the REEs most rocks contain, but also that it was subsequently leached along its fracture flow paths, and lost even more REEs, specifically europium, from those areas. This approach also showed that HREEs were flushed to the center of the PRB, and that gadolinium signatures from ancient oceans can persist for 60Ma. Application of the WBPW and NASC normalization to geothermal systems outside Wyoming could offer confirmation or challenge to the proposed flow path of the water.

7. CONTRIBUTIONS AND ACKNOWLEDGEMENTS

CN and DB drafted, edited, and conceived of the ideas in this manuscript. Water samples were collected by CN. Rock samples were collected by DB. All authors reviewed the chapter manuscript. Contributors include: Tom Moore who prepared figures 2-4, Ghanashyam Neupane who performed the aqueous REE measurement, Yuriy Ganshin who performed the calculations to produce the WBPW, and Matt Johnson who recognized agreement between Nealson et al. (2009) and this work. The authors would like to thank our industry partners who allowed water sample collection, and the landowners who allowed rock collection.

REFERENCES

Alibo D.S., Y. Nozaki. Rare earth elements in seawater: particle association, shale-normalization, and Ce oxidation. *Geochimica et Cosmochimica Acta,* **63(3)**, (1999) pp. 363–372. http://dx.doi.org/10.1016/S0016-7037(98)00279-8

Anna, L.O., Klett, T.R., and Le, P.A., 2009, Total petroleum systems and geologic assessment of oil and gas resources in the Powder River Basin Province, Wyoming and Montana: *U.S. Geological Survey Digital Data Series DDS–69–U*, 3 chaps., 1 CD-ROM. (Revised April 2010)

Blakey, Ron C., 2014, Paleogeography and Paleotectonics of the Western Interior Seaway, Jurassic-Cretaceous of North America: *AAPG Search and Discovery Article #30392* (Accessed fromAAPG.org)

Byrne RH and Sholkovitz ER (1996) Marine chemistry and geochemistry of the lanthanides. In: Gschneider Jr KA and Eyring L (eds) *Handbook on the Physics and Chemistry of Rare Earths*, **vol. 23**, pp. 497-593. https://doi.org/10.1016/S0168-1273(96)23009-0

Condie, K. C., 1993, Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales: *Chemical Geology*, **v. 104**, p. 1–37.

DeBaar Hein. J. W., Brewer P. G., and Bacon M. P. (1985) Anomalies in rare earth distribution in seawater: Gb and Tb. *Geochim. Cosmochim. Acta* **49**, 1961–1969.

Quillinan S., Nye C., Engle M., Bartos T., Neupane G., Brant J., Bagdonas D., McLing T., McLaughlin J. F. (2019). Assessing rare earth element concentrations in geothermal and oil and gas produced waters: A potential domestic source of strategic mineral commodities. *Final Report to U.S. Department of Energy, Geothermal Technologies Office, 184 pages. Award Number: DE-EE0007603*, accessed via https://gdr.openei.org/submissions/1125

De Baar, Hein J.W., Michael P.Bacon, Peter G.Brewer, Kenneth W.Bruland. Rare earth elements in the Pacific and Atlantic Oceans. *Geochimica et Cosmochimica Acta,* **v49** i9 (1985), pp. 1943-1959 Accessed from https://www.sciencedirect.com/science/article/pii/0016703785900894

Gast, P. W. 1960. Limitations on the composition of the upper mantle. *J. Geophys. Res.* **65**, pp. 1287- 1297.

Gromet, L.P., Haskin, L.A., Korotev, R.L. and Dymek, R.F., 1984. The “North American shale composite”: its compilation, major and trace element characteristics. Geochimica et Cosmochimica Acta, **48(12)**, pp.2469-2482.

Hanson, Gilbert N. 1980. Rare Earth Elements in Petrogenetic Studies of Igneous Systems. *Annual Review of Earth and Planetary Sciences*. **Vol. 8**: 371-406. May 1980. https://doi.org/10.1146/annurev.ea.08.050180.002103

Haskin, L. A., Frey, F. A., Schmitt, R. A., and Smith, R. H. 1966. Meteoritic, solar and terrestrial rare-earth distributions. *Phys. Chem. of the Earth VII*, pp. 167-322

Keefer, William R. (1970) Geology of the Wind River Basin, Central Wyoming *USGS Professional Paper 495-D*. Accessed from: https://doi.org/10.3133/pp495D.

McLennan, S.M. (1989) Rare earth elements in sedimentary rocks; influence of provenance and sedimentary processes. *Reviews in Mineralogy and Geochemistry*, **21**, 169–200.

Nealson Philip H., Patrick K. Trainor, and Thomas M. Finn. (2009) Gas, Oil, and Water Production in the Wind River Basin, Wyoming. *USGS Scientific Investigations Report 2008–5225*. https://pubs.usgs.gov/sir/2008/5225/downloads/SIR08-5225.pdf

Nelson, D. T., 2005, Rare Earth Elements as a Natural Tracer of Ground Water Flow in the Eastern Snake River Plain Aquifer, Idaho. *M.S. Thesis: University of Idaho, Moscow, Idaho*.

Nye, C., Bagdonas, D.A., and Quillinan, Q.: A New Wyoming Basin Produced Waters REE Normalization and Its Application, *Proceedings,43nd Workshop on Geothermal Reservoir Engineering*. Stanford University, Stanford, CA (2018). SGP-TR-213. https://pangea.stanford.edu/ERE/db/IGAstandard/record_detail.php?id=28263

Nye, C., Quillinan S., Neupane G., and McLing T. L.: Aqueous Rare Earth Element Patterns and Concentration in Thermal Brines Associated With Oil and Gas Production, *Proceedings,42nd Workshop on Geothermal Reservoir Engineering*. Stanford University, Stanford, CA (2017). SGP-TR-212.

Piper, David Z. and Michael Bau, Normalized Rare Earth Elements in Water, Sediments, and Wine: Identifying Sources and Environmental Redox Conditions, American Journal of Analytical Chemistry (2013) 69-83, http://dx.doi.org/10.4236/ajac.2013.410A1009

Qiu X., C. Liu, F. Wang, Y. Deng, G. Mao. Trace and rare earth element geochemistry of the upper Triassic mudstones in the southern Ordos Basin, *Central China Geol. J.,* **50** (2015), pp. 399-413 https://doi.org/10.1002/gj.2542

Quillinan, Scott., Charles Nye, Mark Engle, Timothy Bartos, Ghanashyam Neupane, Jonathan Brant, Davin Bagdonas, Travis McLing, and J. Fred McLaughlin. Assessing rare earth element concentrations in geothermal and oil and gas produced waters: A potential domestic source of strategic mineral commodities, Final Report to U.S. Department of Energy, Geothermal Technologies Office, Project Number EE0007603. *U.S. Department of Energy Geothermal Data Repository*, Submission #1125, (2019). Accessed from https://gdr.openei.org/submissions/1125

Blakey Ron C., 2014, Paleogeography and Paleotectonics of the Western Interior Seaway, Jurassic-Cretaceous of North America: *AAPG Search and Discovery Article #30392* (Accessed from AAPG.org)

Sverjensky, D.A., 1984. Europium redox equilibria in aqueous solution. *Earth Planet. Sci. Lett*., **67** (1984), pp. 70-78.

Taylor, S. R. 1964. Trace element abundances and the chondritic earth model. *Geochim. Cosmo- chim. Acta* **28**, pp. 1989-1998.

Veil, John, 2015. U.S. Produced Water Volumes and Management Practices in 2012. *Veil Environmental, LLC* pp. 1-119. Accessed from: http://www.veilenvironmental.com/publications/pw/prod_water_volume_2012.pdf

Wolfram Research, Inc. (2018) (www.wolfram.com), Mathematica Online, Champaign, IL. Accessed via: *Periodic Table Table, Theodore Gray (2018)* http://periodictable.com/Properties/A/AtomicRadius.html

(WSGS) Wyoming State Geological Survey (2015). Geologic Cross Sections, Wind River Basin, Wyoming. State Geologist: Thomas A. Drean. Accessed from: http://www.wsgs.wyo.gov/docs/wsgs-web-wrb-xsec.pdf

University of Wyoming. (2017). Rare Earth Geochemistry of Rock Core form WY Reservoirs [data set]. Samples GA18-23505 to GA18-24800. Accessed from http://gdr.openei.org/submissions/926, https://dx.doi.org/10.15121/1360764.