Aqueous Rare Earth Element Patterns and Concentration in Thermal Brines Associated With Oil and Gas Production

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ABSTRACT

This study is part of a joint effort by the University of Wyoming (UW) School of Energy Resources (SER), the UW Engineering Department, Idaho National Laboratories (INL), and the United States Geological Survey (USGS) to describe rare earth element concentrations in oil and gas produced waters and in coal-fired power station ash ponds. In this work we present rare earth element (REE) and trace metal behavior in produced water from four Wyoming oil and gas fields and surface ash pond water from two coal-fired power stations.

The concentration of REEs in oil and gas produced waters is largely unknown. For example, of the 150,000 entries in the USGS National Produced Waters Geochemical Database less than 5 include data for REEs. Part of the reason for this scarcity is the analytical challenge of measuring REEs in high salinity, hydrocarbon-bearing waters. The industry standard for water analysis struggles to detect REEs in natural waters under ideal conditions. The detection of REEs in oil and gas field samples becomes all but impossible with the background noise and interferences caused by high concentrations of non-REE ions and residual hydrocarbons. The INL team members have overcome many of these challenges (e.g. McLing, 2014), and continue to develop their methods.

Using the methods of the INL team members we measured REEs in high salinity oil and gas produced waters. Our results show that REEs exist as a dissolved species in all waters measured for this project, typically within the parts per trillion range. The samples may be grouped into two broad categories analytically, and these categories match their genesis: Wyoming oil and gas brines contain elevated levels of Europium, and Wyoming industrial pond waters show elevation in heavy REEs (HREEs). While broadly true, important variations exist within both groups. In the same field Europium can vary by more than an order of magnitude, and likewise HREEs in industrial ponds at the same site can vary by more than an order of magnitude. Future work will investigate the reasons for these variations.

1. INTRODUCTION

Rare Earth Elements (REEs) are present in almost all rocks and waters in extremely low concentrations. Their average crustal abundance of ~10ppm means REEs are not particularly rare (Rudnick et al. 2003). However, their near-universal occurrence means that REEs do not often reach economically significant concentrations. This makes commercial production of REEs challenging, and increases their value on the market. Market applications include alloys, glasses, tracers, lasers, magnets, diagnostic medicine, geo-spatial sensors, and many modern electronics. Due to the importance of these applications, the Department of Defense (Kendall, 2013) and Department of Energy (Chu, 2011) have released lists of the most important REEs and critical materials. Europium and many HREEs figure prominently on these lists.

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

[1] DOE identified critical material

Figure 1: REEs and trace elements that the DOE identifies as critical materials. The DOE list is ranked (not shown) with some REEs such as Nd, Eu, Tb, Dy, and Er at the top of the list. This study detected many of these elements.

There are very few economical hard-rock deposits of REEs in the world. Most notable among these is the Bayan Obo mine, controlled by the People's Republic of China and affiliated interests. Other hard-rock mines include the closed Mountain Pass mine in California, and potential Bear Lodge mine in north-east Wyoming, both of which could improve the world's REE supply in an appropriately economic situation. Because hard-rock mining suffers challenging economics, this work will describe aqueous REEs, as the first step to possible implementation of aqueous REE mining.

The primary historical obstacle for assessment of aqueous REE resources was their low (ng/L) concentration, and ubiquitous interferences. The present study was made possible by researchers at Idaho National Laboratory (INL) who refined a technique to measure low concentration aqueous REEs reliably despite the presence of interfering compounds (McLing et al., 2014). INL's method has been essential to the present study and paves the way for further studies of dissolved REEs.

2. STUDY AREA

This paper considers two Wyoming basins and two Wyoming power stations for their REE potential, shown on Figure 2. The two basins are the Wind River Basin (WRB), and the Powder River Basin (PRB). The two coal-fired power stations are the Laramie River Station (LR), and the WyoDak Station (WYDAK). The basin waters are co-produced from oil and gas wells, while the waters at the power plants come from on-site ponds and the scrubbers used to remove ash from the plant's exhaust stream.
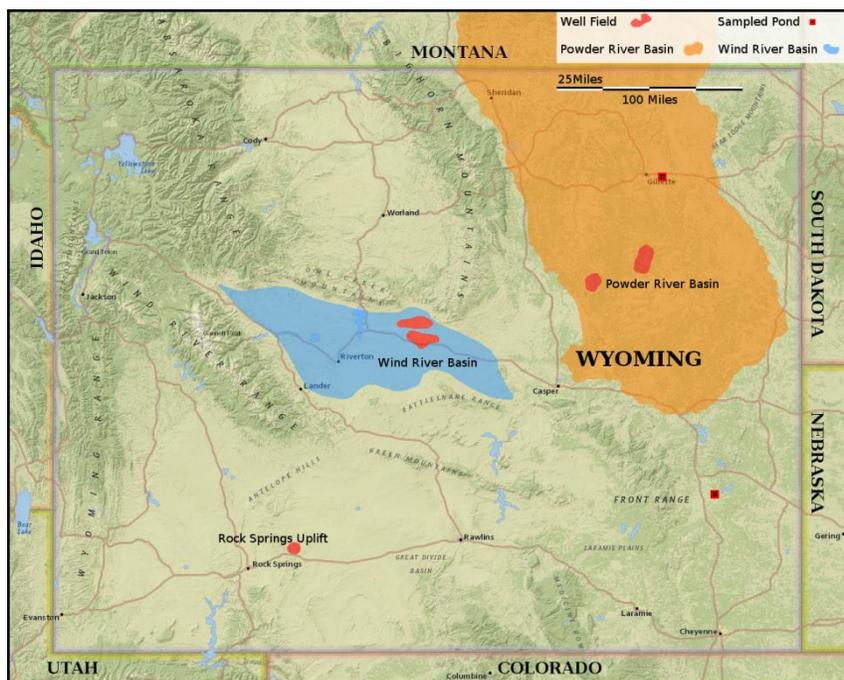
Figure 2: The state of Wyoming, showing the fields (red), and the basins (blue/orange) sampled in this study. The squares mark the location of the two power stations. Note the Rock Springs Uplift (RSU), which is used in the present work to check our conclusions (Mcling et al., 2014).

The WRB covers approximately 8,000mi² (20,500km²) of Central Wyoming. In the WRB, produced water samples were collected from three reservoirs: the Fort Union, the Lower Fort Union-Lance, and the Madison. The fluid in the Fort Union reservoirs is typically ~230°F (110°C) at 5,500ft (1,600m) but can reach ~350°F (175°C) at that depth. The deeper Madison waters exceed 420°F (215°C) at 24,000ft (7,300m). In addition to these produced waters, samples were collected at the inlet and concentrated reject brine outlet of a desalination plant.

The PRB covers approximately 19,500mi² (50,500km²) of North Eastern Wyoming, and South Eastern Montana. (USGS, 2013) This paper considers only the Southern Powder River Basin. In the PRB we collected samples from six formations including: the Parkman, the Shannon, the Niobrara, the Turner, the Frontier, and the Mowry. These formations and basin-axis-relative locations are shown on Figure 3. Temperatures in the PRB include 230°F (110°C) at 10,000ft (3,000m) in the Turner and 240°F (115°C) at 13,500ft (4,100m) in the Niobrara.
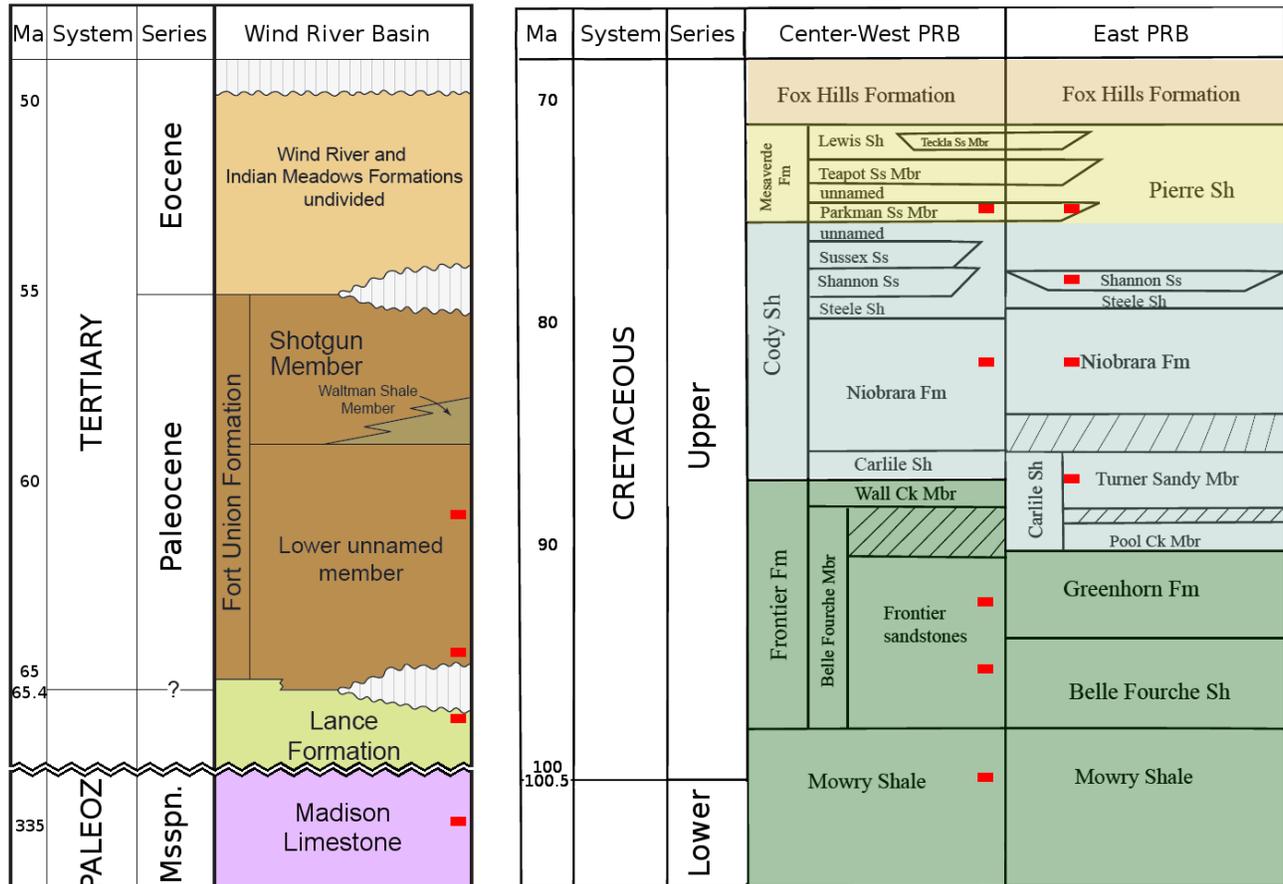
Figure 3: The relevant stratigraphy of the WRB and PRB spanning from Paleocene to Mississippian, and Upper to Lower Cretaceous. Approximate sample location-ages are marked with red boxes. Note that WRB samples vary mainly by depth, and PRB samples vary laterally.

The two coal-fired power plants sampled for this study burn the same coal stock but use different initial water sources. Both Laramie River Station and WyoDak Station use coal mined in the PRB. Both stations in this study do not discharge water but rather evaporate it in long-term ponds after much reuse. This means that Laramie River Station and WyoDak Station should be identical in all significant respects other than initial water source.

3. METHODS

All produced water samples were collected from post-separator outlets. All power station samples were collected by immersion of the bottle in the sampled pond. In both cases the bottles were rinsed with the water to be sampled before final collection and sealing.

All samples were collected in acid-washed, 500mL, Low-Density Poly-Ethylene (LDPE) bottles. These LDPE bottles were transported on dry-ice, and frozen within 8hrs. After overnight freezing, they were thawed, filtered, and split at the lab of the Carbon Management Institute (CMI). During splitting the samples were filtered through a 0.45um mixed cellulose ester filter-paper into a vacuum flask. Part of the filtrate was acidified with trace-metal-grade 70% nitric acid to a pH of <2 and another part retained unacidified. This splitting allows the maximum number of analyses to be performed. Split samples were stored refrigerated and, when necessary, transported on gel-ice.

4. ANALYSIS

Three analyses were performed on the samples to determine cation concentration, anion concentration, and REE concentration. These analyses are in addition to basic field data such as sample temperature at the time of collection, initial pH, and conductivity.

Cations were measured as elements by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The ICP-OES analysis also measured the concentration of selected trace elements. Anions were measured by Ion Chromatograph (IC) exempting carbonate/bicarbonate which was analyzed as alkalinity by an external lab. REE concentration was determined at the parts per trillion (ppt) level by INL using a REE-selective resin and analyzed in triplicate using an Agilent 7500a Inductively Coupled Plasma Mass Spectrometer (IPC-MS), with a Babington nebulizer, and an electron multiplier detector.

5. GEOCHEMICAL BEHAVIOR

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. The TDS of the WRB samples ranges from 6,791 to over 11,780 ppm, not including the water treatment plant which produces a reject brine in excess of 64,907ppm. The pH is slightly basic, averaging 7.6 units.

The water type in all PRB samples is sodium chloride, with very minor contributions from the other major cations, and bicarbonate. Sulfate was not detected in the PRB samples. The TDS of these samples, ranging from 19,049 to 62,725ppm, is greater than the WRB and also more variable because water was sampled from many different formations. The pH of these samples is neutral.
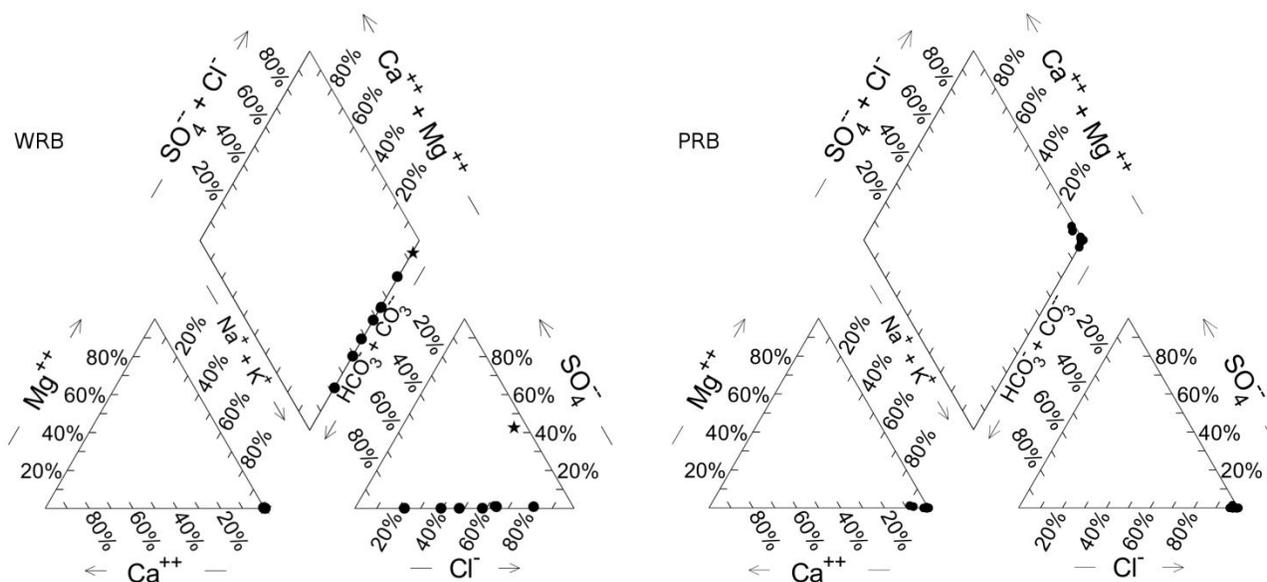
Figure 4: Piper diagrams for the WRB and PRB waters in this study. The PRB is dominated by Na^+ and Cl^- but many samples in the WRB have substantial bicarbonate. The star represents the reject brine of the water treatment plant, which unlike all other samples contains significant sulfate as a result of engineered processes.

Of the well field samples, MD-6 merits special mention because it was collected from the reject brine stream of a desalinization plant rather than an oil and gas well. This plant uses reverse osmosis to purify produced water to the quality needed for surface discharge. The reject brine stream shows the approximately ten-fold increase in concentration resulting from this process, as well as elevated sulfate. The ten-fold increase in concentration of these major ions is not mirrored by REEs, suggesting that REEs were mostly removed during the treatment train.

The water type of the coal-fired power station samples is sodium-sulfate, but contains most major ions as well. The anions chloride and (bi)carbonate are significant in most samples, as are a wide variety of major and minor cations. TDS of the power station ponds is far lower than the produced waters, ranging from 2,454 to 4,631 ppm, with notable exceptions for two non-discharging evaporation ponds at Laramie River Station. Station waters are also more basic than the WRB and PRB produced waters, with a pH between 7.5 and 11. The high pH most likely represents the contribution of lime which is used to clean the flue gas before being disposed with the fly-ash in the holding ponds. Support for this explanation comes from the highest pH sample, WYDAK-25, which samples water from a fly-ash truck.

6. RARE EARTH ELEMENT BEHAVIOR

The concentrations of REEs in Wyoming brine samples are given in Table 1, in the appendix. All samples present a positive europium anomaly, as shown on Figure 4. Large europium anomalies (Eu/Eu* > 4) only occur in oil and gas produced waters. All samples also present a negative cerium anomaly with the exception of two surficial industrial waters (WYDAK-22 and WYDAK-25) with no

anomaly, and one PRB sample (PRB-13) with the only positive cerium anomaly. These europium and cerium anomalies suggest that europium fractionates into the water, and cerium tends to remain in the host reservoir rocks.

Group	Sample	Anomalies		
		Europium	Cerium	LREE/HREE
WRB	MD-2	3.96	0.54	10.12
	MD-3	21.69	0.52	5.62
	MD-4	33.31	0.53	1.81
	MD-5	38.05	0.42	2.19
	MD-6	13.83	0.39	2.46
	MD-7	36.59	0.51	1.90
	MD-8	41.10	0.37	1.22
	LC-31	1.77	0.41	0.07
PRB	PRB-10	15.60	0.28	5.08
	PRB-11	11.42	0.36	7.21
	PRB-12	10.52	0.42	3.92
	PRB-13	9.00	1.41	1.60
	PRB-14	5.19	0.50	0.08
	PRB-15	10.36	0.40	0.01
	PRB-16	6.88	0.32	0.23
	PRB-17	15.66	0.13	0.45
	PRB-18	13.78	0.20	1.82
	PRB-19	4.74	0.37	0.00
Power Stations	WYDAK-22	1.36	1.00	0.03
	WYDAK-23	1.24	0.56	0.02
	WYDAK-24	2.08	0.65	0.11
	WYDAK-25	3.44	1.05	0.03
	LR-27	2.09	0.35	0.29
	LR-28	2.61	0.68	0.40
	LR-29	1.26	0.64	0.90
	LR-30	1.97	0.42	0.23

Figure 4: Enrichment (>1) and depletion (<1) indices for Eu, Ce, and Light to Heavy REEs. The largest europium anomalies are in the WRB. Significant Eu anomalies exist in the PRB also. The most remarkable anomaly at the power stations is their strong HREE enrichment, shown by LREE/HREE values <<1. Anomalies were calculated by: Eu/Eu*, Ce/Ce*, and La/Yb where: Eu*=$\sqrt{(Sm_{NASC} \times Gd_{NASC})}$ and Ce*=$\sqrt{(La_{NASC} \times Pr_{NASC})}$ after Taylor and McLennan, 1995.

Produced waters and surficial industrial waters may present a broad range of LREE-HREE ratios, and cannot be distinguished by those ratios alone. As mentioned above, significant europium enrichment can be used to distinguish produced water from surficial industrial waters. Within the group of produced waters, a significant Gd enrichment indicates that water came from the PRB whereas its absence suggests the other basin in this study, the WRB.

The concentrations of REEs in these brines are within the expected ranges for filtered natural water samples with near-neutral pH (e.g., Wood, 2002; Nelson et al., 2004). Samples collected from ash ponds (e.g., WYDAK-22, WYDAK-23) show a higher concentration of HREEs whereas samples from well fields show higher concentrations of Europium. This observation requires more supporting data, but suggests two distinct modes of REE dissolution fractionation, perhaps caused by the presence or absence of significant sulfate.

North American Shale Composite (NASC) normalized spider plots are shown in Figure 5. Normalization to the NASC shows the results of water-rock interaction. All samples show a positive Eu anomaly, and a slight negative Ce anomaly. These anomalies suggest that Eu from the host rocks naturally dissolves into the water, and Ce has remained in the host rock.
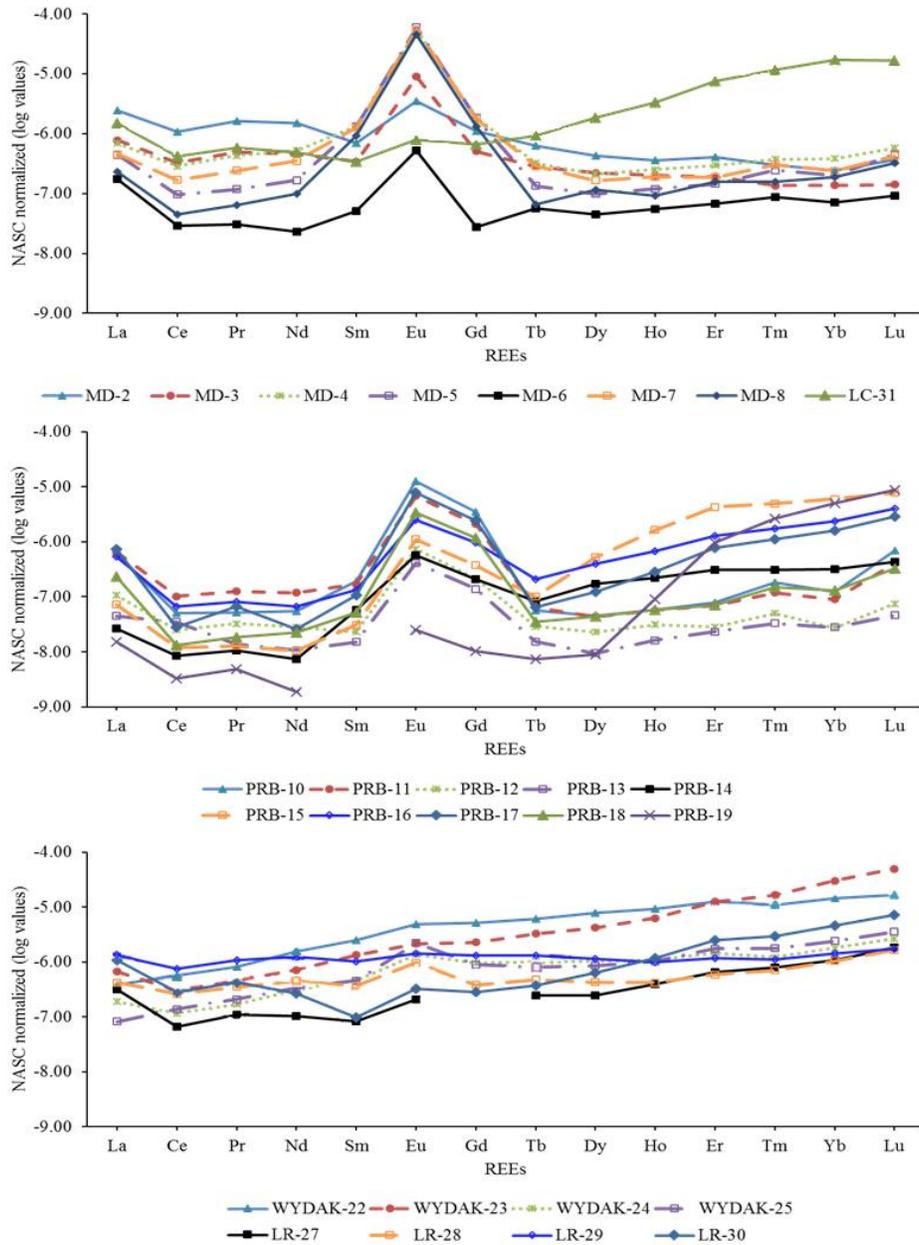
Figure 5: Three NASC-normalized REE diagrams for the WRB, PRB, and power stations in this study. a) The WRB samples come from clastic sandstone reservoirs except for sample LC-31 which comes from a deep carbonate reservoir. b) The PRB samples generally come from rocks of marine genesis, and the high Gd signature of the resevoir transfers to the water. The samples with the greatest HREE concentration come from the field on the axis of the basin. c) The power station samples come from ponds subject to different evaporation ratios, except WYDAK-25 which came from a truck used to collect fly-ash washed off of the scrubber.

The NASC-normalized REE patterns show three general groups. The group from the WRB (Figure 5a) shows the strongest Eu anomaly (Figure 4) and a slight enrichment of LREEs. The PRB group (Figure 5b) exhibits an Eu anomaly nearly as strong as the WRB group and HREE enrichment in samples from the field on the basin axis. The final group (Figure 5c), from the power station ponds, has the smallest Eu anomaly, but very regular enrichment of HREEs over LREEs (Figure 4).

The strongly positive Eu anomaly identified for the WRB and PRB brine samples indicates that these brines are sourced from a reducing environment (Table 3). In nature Eu can exist in divalent or trivalent state. In reducing conditions the easily dissolved divalent state is more common than the trivalent state (Sverjensky, 1984). Because of this behavior water-rock reactions in a reducing environment will enrich Eu over other redox-insensitive REEs. This behavior is also found in some groundwater samples from reducing environments in China (Guo et al., 2010).

While NASC normalization offers insight to REE behavior in water-rock reactions, normalization to North Pacific Deep Water (NPDW) offers a comparison of water to water. When normalized to NPDW REE values less than 1 are lower concentrations than found in the ocean, and those greater than 1 exceed reported oceanic concentrations. Using the ocean as a reference point is important because ocean mining of critical materials has been suggested and seriously considered for over half a century (Davies et al., 1964). Ocean mining is a comparable technology in direct competition with extraction of REEs from the sources considered here. This means that to be competitive, the present sources must at a minimum exceed ocean concentrations, unless their economics are improved for some other reason.
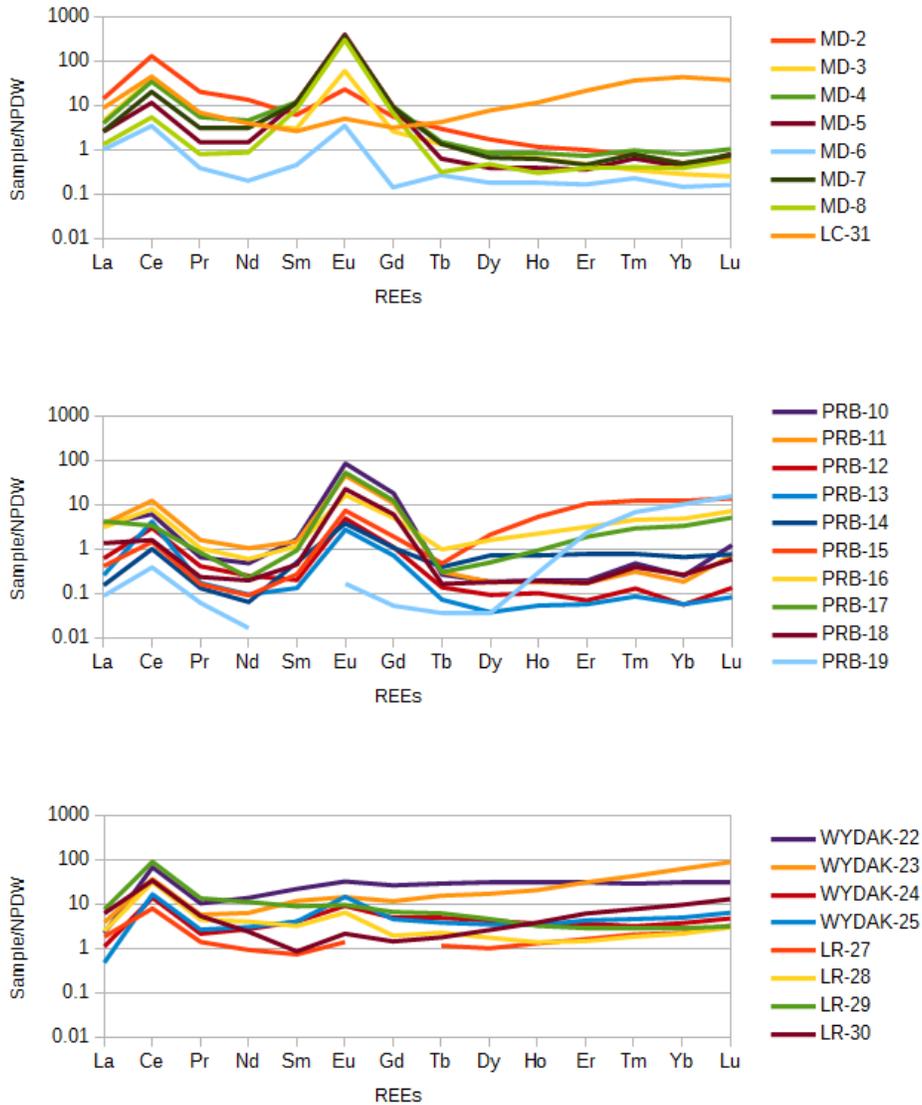
Figure 5: Three NPDW-normalized REE diagrams for the WRB, PRB, and power stations in this study. a) The WRB samples contain more LREEs and Eu than the oceans, but lower HREEs. b) The PRB samples contain more Eu and Gd than the oceans and in some cases more HREEs c) The power station samples are generally flat, indicating similarity to ocean water, but have a marked HREE enrichment and the highest concentrations of the critical REEs Tb, Dy, and Er found in this study.

Many conclusions from the NASC also apply to the NPDW. Wyoming oil and gas field samples regularly contain Eu in concentrations around 100 times greater than ocean water. Select produced waters, especially those from deep carbonate reservoirs, have about 10 times the HREEs in the ocean. The power station samples are similar to ocean water, but more concentrated, suggesting that processes designed to mine oceans may leverage the pre-concentration of these station waters.

Although NPDW normalization makes comparison with ocean mining simpler, it introduces a positive Ce anomaly. This anomaly results from naturally occurring adsorption and oxidation of Ce in the ocean (Alibo and Nozaki, 1999). Because nearly all non-ocean waters will show such an anomaly it should be considered of low-importance, especially given Ce's current status as one of the less important REEs.

7. DISCUSSION

The REEs in waters from the WRB, PRB, and power stations exhibit different behavior. The high bicarbonate WRB is enriched in LREEs and Eu. The high chloride PRB is enriched in Gd and, for samples on the basin axis, HREE enriched. The high sulfate power stations exhibit a steady HREE enrichment with insignificant Eu or Gd anomalies. This suggests that the nature of REE mobilization depends upon the local conditions, available ligands, and source of REE, be it country rock or coal by-products.

Informed by the observations of Migdisov et al. (2016) we constructed a formula to relate the relative importance of common anion ligands to the total rare earth element concentration.

$$(0.05 \bullet Alk) + (0.01 \bullet Br) + (0.001 \bullet Cl) = R$$

(1)

where *Alk, Br, Cl,* and *R* are the concentrations of alkalinity as CaCO3, bromide ions, and chloride ions in ppm, and total rare earth elements from lanthanum to lutetium in ppt, respectively. The coefficients were chosen based on the best-fit line for the three ligand species versus total REEs.

The resultant graph when this formula is applied to produced waters is shown in Figure 6. As we continue to collect new samples we will add them to this plot to see if the formula continues to hold. We hope to expand this relationship to include the effects of pH and other known ligands such as sulfate. These expansions should allow fitting of surficial pond water data which at present fit the formula very poorly (not shown). Note that two PRB samples with incomplete geochemistry are also not shown. Similarly the engineered water, MD-6, from the water treatment plant reject stream is not shown.
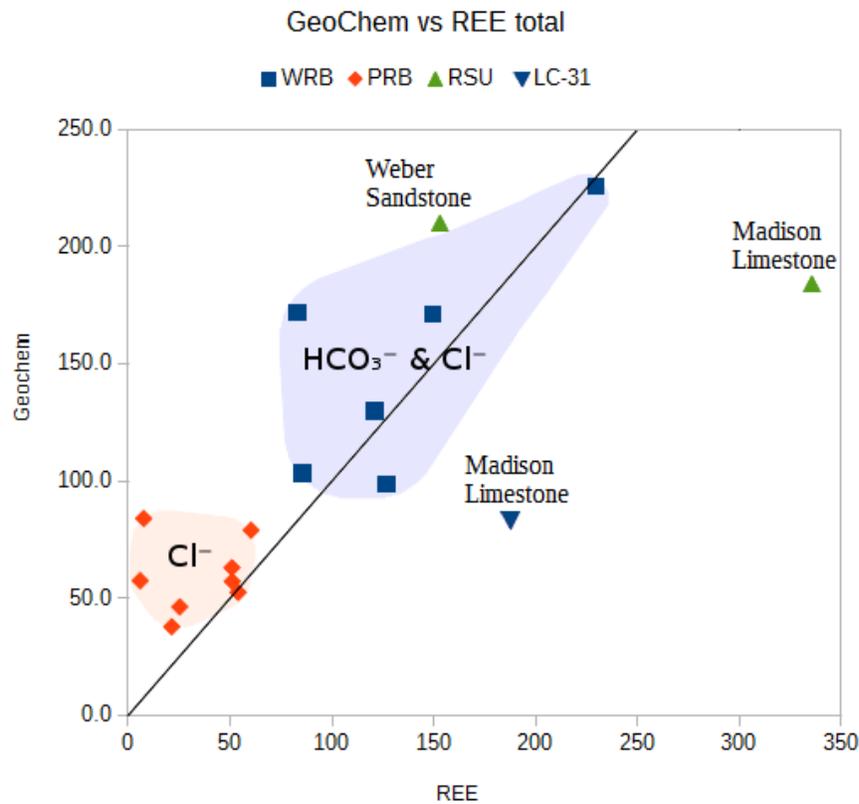
Figure 6: A graph of the result of applying our first attempt at a formulaic relationship between ligands and total REEs. The good fit of the present relationship is mostly due to the abundance of bicarbonate in the WRB (blue), which allows those data to be fit independently of the chloride-dominated PRB (orange). The two green data points are from an early study by our team of the Rock Springs Uplift (McLing et al., 2014).

Because the RSU samples were not used in formulation of the suggested trend, they offer a way to check the trend's relevance. The clastic Weber is in agreement, however the carbonate Madison lies significantly off the prediction. One possible explanation is that carbonates are affected by an additional variable which our simplistic model neglects. This explanation is supported by the other Madison sample from the WRB (blue triangle). Because both Madison formations contain water with greater REEs than expected, another, unconsidered, ligand could be the variable needed in carbonate formations. Collection of more samples from carbonate formations might confirm this hypothesis.

8. CONCLUSIONS

This study showed that REEs are mobile in all of the sampled aqueous systems at the ng/L level. As confirmed by field and method blanks, the concentration of REEs can be accurately measured in geothermal waters by the methods of McLing, et al., 2014. This study also showed that the REEs carry different patterns depending on which of two Wyoming basins they source from. The distinct patterns raise the possibility of using REEs as a naturally occurring tracer. With future work we will improve our ability to interpret these patterns.

Application of Migdisov et al. (2016), though admittedly generalized, nevertheless results in permissive evidence for Migdisov's interpretation of ligand-dominated mobility. As work progresses, we will check new samples for agreement with the proposed relationship, and if necessary revise or discard the relationship.

Produced geothermal waters can be readily distinguished from surficial waters by their Eu anomaly. The higher concentration of this valuable rare earth element makes them attractive for further value-added research. Such value-added processes could include mining the input or output water to a geothermal power station.

9. FUNDING SOURCES AND CONFLICT OF INTEREST

The present project was seed-funded by the state of Wyoming. Subsequent funding came from the DOE at the federal level. This model of using state-initiated studies to reduce risk and allow larger scale follow-up from federal agencies appears to address the interests of all participants in the research process.

The authors declare no conflict of interest.

APPENDIX

Tables 1, 2, and 3 report the water chemistry data measured in the WRB, PRB, and Power Station samples, respectively. All units are ppm, except where noted as °C or unit-less. Some critical materials are present in addition to the REEs in these samples. Lithium figures prominently in the PRB.

Elements in mg/L	Ft Union MD-2	U Ft Union MD-3	Ft Union MD-4	Input MD-5	Reject MD-6	Ft Union MD-7	Ft Union-L MD-8	Madison LC-31
Alkalinity, Total as CaCO3	4,500	3,410	3,390	2,550	4,950	1,930	2,020	1,830
Bromide (Br)	3	15	11	17	134	13	15	ND
Calcium (Ca)	1	16	18	22	3	17	20	2
Chloride (Cl)	633	1,190	1,550	2,040	19,600	2,030	2,060	8,350
Fluoride (F)	1.3	1.0	1.8	1.8	10.0	2.1	2.0	6.6
Magnesium (Mg)	ND	13	3	3	ND	2	2	ND
Nitrogen, (N) Ammonia as N	8.6	42.0	9.9	5.5	6.4	3.7	5.2	45.0
Potassium (K)	40	57	27	23	183	17	18	56
Sodium (Na)	2,590	3,510	2,480	2,500	23,200	2,200	2,160	379
Sulfate (SO4)	ND	5	4	ND	19,700	15	ND	ND
Barium (Ba)	0.5	23.5	7.4	5.9	0.1	3.5	4.3	0.2
Boron (B)	7.3	3.8	9.1	11.2	82.7	10.1	11.8	10.1
Iron (Fe)	0.3	0.2	0.1	0.1	0.1	0.1	0.1	ND
Lithium (Li)	2.5	3.8	2.2	1.8	13.8	1.2	1.4	1.4
Phosphorus (P)	ND	0.4	ND	0.3	4.9	ND	0.4	ND
Silicon (Si)	3.5	27.7	35.5	39.1	164.0	38.4	35.7	4.0
Strontium (Sr)	0.1	0.8	1.0	1.2	0.1	0.9	1.1	0.3
pH (units)	9.6	7.2	7.3	7.0	10.0	7.6	7.3	6.5
TDS (ppm)	7,564	9,311	8,566	8,228	64,907	6,791	6,999	11,780
Temperature (°C)	11.0	36.0	25.2	29.6	35.3	65.4	52.1	20.0

Table 1: Geochemistry of the WRB samples. "U Ft Union" indicates the upper Fort Union reservoir. "Ft Union-L" indicates the Fort Union-Lance reservoir.

Elements in mg/L	Niobrara PRB-10	Turner PRB-11	Parkman PRB-12	Turner PRB-13	Parkman PRB-14	Mowry PRB-15	Niobrara PRB-16	Shannon PRB-17	Frontier PRB-18	Frontier PRB-19
Alkalinity, Total as CaCO3	268	267		323	1,440	425	256	519	219	223
Bromide (Br)		355		349	89	293	558	714	261	398
Calcium (Ca)	734	2,290	83	2,340	60	1,680	814	386	1,770	2,560
Chloride (Cl)		35,600		37,800	11,100	33,000	44,600	45,900	24,300	31,200
Fluoride (F)		0.5		0.5	1.9	1.0	1.0	0.8	0.7	0.5
Magnesium (Mg)	72	180	9	171	13	98	74	56	72	127
Nitrogen, (N) Ammonia as N		44.0		49.0	11.5	33.0	63.0	28.0	31.0	38.0
Potassium (K)	95	208	115	1,170	258	76	79	119	181	245
Sodium (Na)	13,000	22,300	5,100	20,100	5,970	15,900	13,700	17,000	13,200	15,500
Sulfate (SO4)		ND		ND	ND	ND	ND	ND	ND	ND
Barium (Ba)	83.9	246.0	8.9	204.0	14.4	42.1	65.1	177.0	113.0	145.0
Boron (B)	22.9	15.7	9.8	19.0	11.2	30.5	29.8	17.7	13.6	11.0
Iron (Fe)	2.0	12.7	4.5	57.3	0.4	1.6	25.0	5.6	0.9	26.6
Lithium (Li)	5.9	14.6	0.8	14.4	0.9	8.9	6.7	5.1	10.2	11.1
Phosphorus (P)	0.8	ND	19.2	ND	1.6	1.8	14.6	5.6	1.8	ND
Silicon (Si)	6.0	42.1	17.1	47.5	22.7	73.3	68.6	37.7	55.0	34.7
Strontium (Sr)	64.0	171.0	7.9	164.0	12.3	111.0	84.9	87.8	135.0	187.0
pH (units)	7.3	6.9	7.9	6.8	7.7	7.0	6.5	6.9	6.6	6.7
TDS (ppm)		59,509		60,515	19,049	50,311	58,386	62,725	39,364	49,100
Temperature (°C)	16.7	34.6	52.3	53.4	50.4	40.0	40.0	34.0	34.0	44.0

Table 2: Geochemistry of the PRB samples. Samples PRB-10 and PRB-12 were volume-limited, so not every analysis was possible. Due to the complexity of produced water, acceptable charge-balance was not achieved in PRB-16 and PRB-17.

Elements in mg/L	1st pond WYDAK-22	Old pond WYDAK-23	2nd pond WYDAK-24	Ash Truck WYDAK-25	Non-D pond LR-27	2nd pond LR-28	1st pond LR-29	Non-D pond LR-30
Alkalinity, Total as CaCO3	275	148	54	72	578	48	37	194
Bromide (Br)	4	5	9	158	116	ND	2	93
Calcium (Ca)	180	459	344	145	507	198	232	385
Chloride (Cl)	765	547	522	1,050	18,600	199	225	2,250
Fluoride (F)	2.3	0.2	0.8	1.0	94.0	0.6	0.4	37.0
Magnesium (Mg)	33	151	40	1	5,430	9	6	1,510
Nitrogen, (N) Ammonia as N	0.5	ND	0.1	ND	18.0	0.2	0.2	13.0
Potassium (K)	29	45	50	48	2,190	60	70	485
Sodium (Na)	945	840	824	1,310	19,200	549	624	4,950
Sulfate (SO4)	1,200	2,430	1,840	1,880	88,200	1,400	1,590	14,500
Barium (Ba)	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1
Boron (B)	1.6	1.2	1.4	1.1	28.4	1.2	1.3	6.0
Iron (Fe)	0.2	0.1	0.0	ND	ND	ND	ND	0.1
Lithium (Li)	ND	ND	ND	ND	4.5	ND	ND	1.5
Phosphorus (P)	ND	ND	ND	ND	ND	ND	ND	ND
Silicon (Si)	2.1	4.0	2.3	2.4	ND	ND	ND	7.0
Strontium (Sr)	3.6	5.4	5.3	3.8	25.4	6.4	7.8	2.9
pH (units)	8.7	7.5	9.1	10.9	8.4	8.4	9.4	7.9
TDS (ppm)	3,458	4,619	3,660	4,631	125,735	2,454	2,778	23,896
Temperature (°C)	14.5	10.3	12.4	14.3	3.5	5.3	4.8	3.5

Table 3: Geochemistry of the Power Station samples. "Non-D" indicates a non-discharging pond, where water only leaves by evaporation. Most ponds are recirculated during normal operation.

REFERENCES

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

Chu, Steven.: Critical Materials Strategy, Department of Energy, Office of International Affairs, Washington, DC (2011). Accessed from: https://energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf (December, 2016)

Davies, R.V., J. Kennedy, K.M. Hill, R.W. McIlroy, R. Spence, (1964). Extraction of Uranium from Sea Water. Nature, Volume 203, 1964, Pages 1110–1115. http://dx.doi.org/10.1038/2031110a0

Guo, H., Zhang, B., Wang, G., & Shen, Z. (2010). Geochemical controls on arsenic and rare earth elements approximately along a groundwater flow path in the shallow aquifer of the Hetao Basin, Inner Mongolia. Chemical Geology, 270(1), 117-125.

Kendall, Frank: Strategic and Critical Materials 2013 Report on Stockpile Requirements, Department of Defense, Defense Logistics Agency, Fort Belvoir, VA (2013). Accessed from: http://www.dla.mil/HQ/Acquisition/StrategicMaterials/Reports.aspx (December, 2016).

McLing, T.L., Smith, W.W., and Smith R.W., 2014 Utilizing REEs as Tracers in High TDS Reservoir Brines in CCS Applications. Energy Proceedia, Volume 63, 2014, Pages 3963–3974

Migdisov A., A.E. Williams-Jones, J. Brugger, F.A. Caporuscio. (2016) Hydrothermal transport, deposition, and fractionation of the REE: experimental data and thermodynamic calculations. Chemical Geology, 439, pages 13–42. http://dx.doi.org/10.1016/j.chemgeo.2016.06.005.

Nelson, B. J., Wood, S. A., & Osiensky, J. L. (2004). Rare earth element geochemistry of groundwater in the Palouse Basin, northern Idaho–eastern Washington. Geochemistry: Exploration, Environment, Analysis, 4(3), 227-241.

Nozaki Y. (2001). Rare Earth Elements and their Isotopes in the Ocean. Encyclopedia of Ocean Science, Academic Press, 2001, pp. 2354-2366. http://dx.doi.org/10.1006/rwos.2001.0284.

Rudnick,R. L., Gao, S., Heinrich,D. H., ,and Karl, K. T., 2005. Composition of the Continental Crust, Treatise on Geochemistry. Oxford, Pergamon. 1–64.

Sverjensky, D. A. (1984). Europium redox equilibria in aqueous solution. Earth and Planetary Science Letters, 67(1), 70-78.

U.S. Geological Survey, 2013, Assessment of Coal Geology, Resources, and Reserve Base in the Powder River Basin, Wyoming and Montana: U.S. Geological Survey Fact Sheet 2012–3143, February 2013. Accessed from: https://pubs.usgs.gov/fs/2012/3143/fs-2012-3143.pdf.

Wood, S. A. (2002). Behavior of Rare Earth Element In Geothermal Systems; A New Exploration/Exploitation Tool (No. DOE/ID13575). University of Idaho (US)