

Rare Earth Elements in North Dakota Lignite Coal and Lignite-Related Materials

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Rare earth elements (REE) are crucial materials in an incredible array of consumer goods, energy system components, and military defense applications. However, the global production and entire value chain for REE is dominated by China, with the U.S. currently 100% import reliant for these critical materials. Traditional mineral ores including those previously mined in the U.S., however, have several challenges. Chief among these is that the content of the most critical and valuable of the rare earths is deficient, making mining uneconomical. Further, the supply of these most critical rare earths is nearly 100% produced in China from a single resource that is only projected to last another 10–20 years. The U.S. currently considers the rare earths market an issue of national security. It is imperative that alternative domestic sources of rare earths be identified and methods developed to produce them. Recently, coal and coal byproducts have been identified as one of these promising alternative resources. This paper details the results of a study on characterization of North Dakota lignite and lignite-related feedstocks as an assessment of their feasibility for REE recovery. The abundance, distribution, and modes of occurrence of the REE in the samples collected were determined in this initial study to inform the selection of appropriate extraction and concentration methods to recover the REE. Materials investigated include the lignite coals, clay-rich sediments associated with the coal seams, and materials associated with a lignite beneficiation system and power plant. The results show that high REE levels exist both in lignite coals and associated sediments. The form of the REE in the clay materials is primarily as ultrafine mineral grains. In the lignite coals, approximately 80–95% of the rare earths content is organically associated, primarily as coordination complexes. [DOI: 10.1115/1.4039738]

1 Introduction

Rare earth elements (REE) include a group of elements with atomic numbers from 57 to 71, making up the lanthanide series of elements consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Yttrium (Y) and Scandium (Sc) are often included in the group because of their similar properties, and have been included in this study. Groupings into light REE (LREE) and heavy REE (HREE) are generally accepted according to the molecular weight, with this study defining LREE to include La through Sm and HREE to include Eu through Lu as well as Sc and Y. Pm is radioactive and is not found in natural settings.

The term “rare earth elements” is actually a misnomer. REE are quite abundant within the earth’s crust, falling in approximately the 50th percentile of elemental abundances [1], and in fact are about 200 times more abundant than gold [2]. The name originated from their discovery in the 18th century, where at the time they were discovered with a class of oxides called “earths” and the elements were presumed to be quite scarce.

Rare earth elements have sometimes been known as “chemical vitamins” because combining very small amounts with other materials can result in vastly different properties. According to the 2014 American Chemistry Council REE Report [3], despite the small volume of REE used in industry, literally hundreds of

billions of products are made possible by rare earths, which are a critical and essential element in many advanced technologies. According to the U.S. Department of Energy National Energy Technology Laboratory (DOE NETL) [4], the REE provide significant value to our national security, energy independence, environmental future, and economic growth. Due to their unique properties that include magnetic, luminescent, and electrochemical properties, the REE make technologies perform with reduced weight, emissions, and energy consumption, or give them greater efficiency, performance, miniaturization, speed, durability, and thermal stability [3]. Major market segments that rely on REE-based products or technologies include health care, transportation and vehicles, lighting, renewable energy systems, communications systems, audio equipment, military defense technologies, and modern electronics. In recent years, the markets for rare earths have been shifting from the more mature applications mainly for the LREE, such as catalysts, to more high-tech newer applications mainly for the HREE, such as permanent magnets that are used in wind turbines and hybrid/electric vehicles.

According to Henderson et al. [5], the REE have long been recognized as useful because of their unusual chemical and physical properties, but their natural occurrence is strongly dependent on geological circumstances, and only in a few locations are they found in sufficient quantity and concentration, and in a suitable form and setting, to make their extraction and exploitation economically viable. Rare earth ores are the result of the concentration of REE either in igneous rocks or in sediments such as sand or clay. Primary rare earth ores contain REE concentrated in minerals through magmatic processing such as partial melting, fractional crystallization, and metasomatism, while secondary rare earth ores are formed from weathering and transportation

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sedimentary processes [6]. There are about 200 known minerals containing REE [7], however, commercial production of rare earths is primarily from six sources, as identified below [8]. Of these, the first three—bastnasite, monazite, and xenotime—are the most important sources [9], making up about 95% of the world's known reserves for REE [10].

- bastnasite [(Ce,La)(CO₃)F],
- monazite [(Ce,La)PO₄],
- xenotime (YPO₄),
- loparite [(Ce,Na,Ca)(Ti,Nb)O₃]
- apatite [(Ca,REE,Sr,Na,K)₃Ca₂(PO₄)₃(F,OH)], and
- ion-adsorption clays.

In recent years, due to their recognition as crucial materials for a large variety of important end use applications including military defense systems, provision of secure sources of REE and REE-based products has been considered by many an issue of national security. Recently, several groups have performed strategic or critical materials assessments that included evaluation of REE. An example is the 2011 study by the U.S. Department of Energy [11], in which mineral commodities were evaluated for their criticality based on a combination of their supply risk and their importance to energy applications. From this analysis, the only elements deemed critical are some of the REE, namely Dy, Nd, Tb, Eu, and Y. Other sources have included Er in the list of critical REE [12]. Very recently, in response to President Trump's executive order [13], the U.S. Geological Survey issued a list of 35 minerals that are deemed critical to the U.S. national security and economy. Among the list were the REE [14].

China has two major REE deposits and has dominated the global supply market over the last two decades [15]. China's principal deposit for the LREE is the Bayan Obo mine, which produces REE as a byproduct of iron ore [16]. China also has a unique deposit, ion-adsorbed clays that are rich in HREE, and critical REE. These types of clays were formed due to weathering of granite source rocks. During weathering, the REE were leached and became fixed as ion-exchangeable cations on the surface of clays [17]. The ion-adsorbed clays located in southern China are unique due to their enrichment in the HREE compared to conventional REE mineral ores and simple and low-cost extraction.

In 2010, China temporarily restricted exports to Japan, which resulted in huge increases in REE prices peaking in 2011 due to supply fears from the rest of the world. As a result, production at the California-based Mountain Pass Mine was restarted after several years of dormancy. However, after peaking in price in 2011, prices have dropped substantially to slightly above 2010 levels, challenging the profitability of non-China-based production, which consists mainly of hard-rock deposits that are deficient in critical REE and HREE. Seredin and Dai [12] noted that mining of the Mountain Pass and similar resources will neither mitigate the crisis in REE resources nor eliminate the shortage of the most critical REE, but will only result in overproduction of excessive Ce.

According to the USGS 2017 Mineral Commodity Summary report [15], China accounted for about 83% of the total global REE supply in 2016, down from about 95% prior to 2010. Meanwhile, the U.S. production was zero, with the Mountain Pass mine having declared bankruptcy and closing operations in the last quarter of 2015. The U.S. is currently 100% import reliant for REE. Although still dominating global supply of HREE, Chegwidden and Kingsnorth [18] have estimated that the Chinese ion-adsorbed clays resource will only last another 15–20 years based on estimated remaining reserves [17,19], and others estimate depletion by 2025 or sooner [20]. The Chinese clays represent essentially the entire global supply of HREE and most of the critical REE [21]. Further, the bulk of Chinese reserves and production is from the Bayan Obo mine that contains only trace amounts of HREE (98.7% LREE), and supplies roughly 80% of the global LREE demand [6]. Due to its limited supply, and because the Chinese clay resource is rich in HREE and critical REE, while

most other traditional resources are deficient in these less common and more valuable elements, it is imperative that new domestic sources of REE, especially the HREE and critical REE, be identified and processes be developed to produce them. Coal and coal byproducts have recently been identified as one of these potential new resources for REE.

2 Background—Rare Earth Elements in Coal and Coal Byproducts

The concentration of rare earth elements in some coals and surrounding sediments can be enriched beyond that found in the earth's crust. However, up until recently, these coal resources were not widely evaluated or considered as possible sources for REE, as the mining industry that was focusing on traditional mineral ore deposits was deemed sufficient to supply world demand indefinitely. However, things have changed in the last decade, with new (and growing) demand for the less common HREE, and with the REE value-chain dominance by China, as well as dwindling supplies of its major HREE resource.

Seredin and Dai [12] have proposed a method of resource assessment for evaluating the suitability of coal (or coal ash) as a source for REE recovery. They have established a total REE (TREE) cutoff of between 800 and 1000 ppm rare earth oxide content in the coal ash, depending on seam thickness as well as the parameters shown below:

- Outlook Coefficient (Coutl): Ratio of critical (Nd, Eu, Tb, Dy, Er, Y) to excessive REE (Ce, Ho, Tm, Yb, Lu).
- Percentage of Critical Elements in total REE (REYdef,rel%).

Based on their extensive database, Seredin and Dai created the plot shown in Fig. 1, which compares various global coal ashes (black diamonds) to some traditional mineral deposits using the

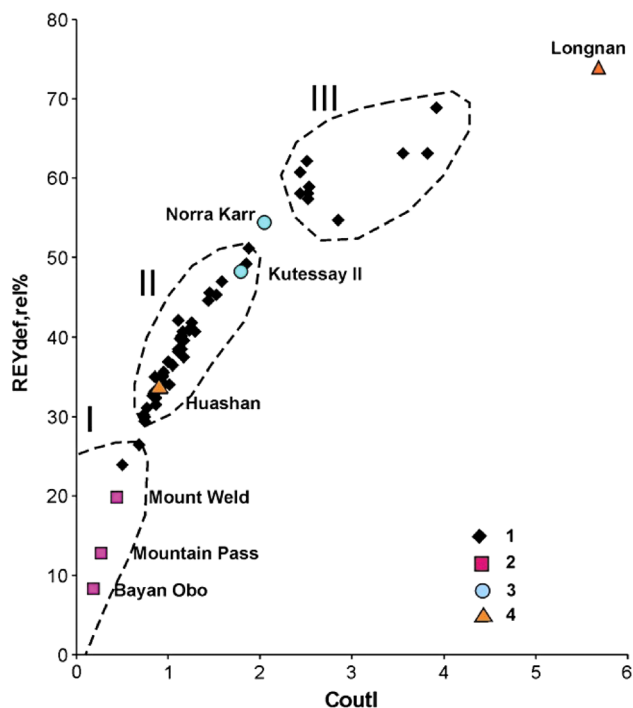


Fig. 1 Classification of REE-rich coal by outlook for individual REE distribution in comparison with selected deposits of conventional types. 1—REE-rich coals; 2—carbonatite deposits; 3—hydrothermal deposits; 4—weathered crust elution-deposited (ion-adsorbed) deposits. Clusters of REE-rich coal distinguished by outlook for REE distribution (numerals in figure): I—unpromising, II—promising, and III—highly promising. Reproduced with permission from Seredin and Dai [12]. Copyright 2012 by Elsevier.

Table 1 Analytical methods used for sample characterization

Category	Equipment	Function
Bulk chemical composition	ASTM standard analysis	Proximate analysis; ultimate analysis; ash composition
	X-ray fluorescence	Bulk chemistry; major, minor, and trace element
	Inductive coupled plasma-mass spectrometry	Abundance of trace elements including REE
REE modes of occurrence	Scanning electron microscopy	Morphological analysis—imaging and chemical composition of minerals
	Chemical fractionation	CCSEM—chemical composition, size and associations (included or excluded relative to coal particles) Quantitatively determine the modes of occurrence of the inorganic elements

above parameters. From the data, they have prepared three clusters of groupings that represent “unpromising,” “promising,” and “highly promising” REE content distributions. Moving up and right on the plot skews the distribution more toward the critical REE, and would indicate a more promising resource. The first cluster contains the well-known mineral ore deposits that contain almost exclusively LREE, and together produce the large majority of global REE supply. These are considered unpromising according to this method. The second and third clusters contain many coals worldwide. The most promising resource identified here is the Longnan ion-adsorbed clay deposit in Southern China, which is currently almost the exclusive global supplier for HREE and most of the critical REE. As described previously, the Chinese clay resources are uniquely enriched in the HREE. Seredin and Dai have concluded that coal, and in particular coal ashes, represents more promising resources for REE than most existing mineral ore deposits.

According to the Energy Information Administration data [22], the U.S. ranks only behind China in total coal production, at about 900,000 thousand short ton in 2015. In terms of total reserves, the U.S. leads the world by a significant margin, with over one quarter of the world’s proven reserves [23]. North Dakota by itself hosts the single largest deposit of lignite known in the world at an estimated 351×10^9 ton, with about 25×10^9 ton of that being economically mineable [24]. Ackman et al. [21] performed a detailed assessment of the prospects of coal and coal byproducts as alternative resources for REE production in the U.S. and found that “unintended production” of REE associated with coal mining potentially exceeds 40,000 ton annually, of that the HREE may exceed 10,000 ton annually, both of which significantly exceed U.S. annual consumption [15]. They estimated that total recoverable reserves of REE in coal may exceed 2×10^6 ton for the major coalbeds and formations in the U.S. In addition to this, the existing coal mines have already absorbed the cost of mining and in many cases also the cost of transportation, crushing, grinding, and coal cleaning. Therefore, there may be opportunities for value-added recovery of REE in several locations throughout the coal utilization value chain. For example, waste streams produced during the coal preparation/cleaning processes may be enriched in REE or other valuable metals as compared to the as-mined coal and would be attractive targets.

3 Sampling of North Dakota Lignite and Lignite-Related Materials

The work conducted in this study focused mainly on samples from the Falkirk Mine and the Coal Creek Station power plant, both near Underwood North Dakota. The Coal Creek Station is an 1100 MW_e PC-fired facility that burns North Dakota lignite from the adjacent Falkirk Mine. Coal Creek Station also uses a unique lignite drying and beneficiation system based on the DryFining™ technology, which both partially dries the fuel and separates some of the undesirable constituents that contain sulfur and mercury. At the mine, samples consisted of the coal seams themselves, as well as the associated clay-rich sediments contained in the roof, floor, and partings. The sampling focused on the Hagel Beds, which contains three seams, the Hagel A, B

Rider, and Hagel B. At the power plant, samples were collected representing the DryFining process streams, as well as combustion bottom ash and fly ash. In addition to the work at the Falkirk Mine and Coal Creek Station, additional samples were provided through the work of Kruger et al. [25] of the North Dakota Geological Survey (NDGS) from several outcroppings of the Harmon-Hanson coal zone and other locations in Southwestern North Dakota. The Harmon-Hanson coals currently have no active mines. Samples collected from the Harmon-Hanson zone represent coals as well as clay-rich materials taken from the margins of the coals and the roof/floor sediments. The Kruger et al.’s [25] report contains details of the sampling locations, local geologies, and sampling methods. A detailed report summarizing the geology of the Fort Union coals in North Dakota and the surrounding region was previously put together by the U.S. Geological Survey [26]. More information about the Hagel and Harmon-Hanson coal zones can be found there. Overall, nearly 200 unique samples were collected in this study.

4 Sample Characterization

The samples collected were analyzed in multiple ways to determine bulk chemical composition and modes of REE occurrence, as summarized in Table 1. The workhorse analytical method used in this study was inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS method has been described in detail by Bank et al. [27], and has become the standard method for determination of the abundance of REE in coal and coal-related samples. Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS) was used to provide magnified images and point chemical composition. Computer controlled SEM (CCSEM) was also used to provide automated analysis of thousands of particles in a sample, and was used to determine chemical composition and particle size of REE-bearing mineral grains.

A sequential solvent extraction method, chemical fractionation [28], was also used to provide quantitative measurement of the modes of REE occurrence in the samples. Chemical fractionation was developed to determine the modes of occurrence of trace elements in low-rank coals, based on the extractability of the elements in solutions of water, 1 molar ammonium acetate, and 1 molar hydrochloric acid. This type of analysis is especially important for low-rank coals that can have significant quantities of organically bound elements, which are ionically dispersed within the organic matrix of the coal and are essentially invisible to SEM and mineralogical techniques. A 75 g sample of $-45 \mu\text{m}$ (-325 -mesh) vacuum-dried coal is stirred with 160 mL of deionized water to extract water-soluble minerals such as sodium chloride or sodium sulfate. After being stirred for 24 h at room temperature, the water-coal mixture is filtered. The filtered coal is dried, and a portion is removed to be tested by ICP-MS to determine the concentration of each element remaining. The residues are then mixed with 160 mL of 1 molar ammonium acetate (NH_4OAc) and stirred at 70°C for 24 h to extract the elements associated with the coal as ion-exchangeable cations present primarily as the salts of organic acids. The ammonium acetate extractions are performed two more times to effect complete removal of the ion-exchangeable cations. After the third

ammonium acetate extraction, a sample of the dried residue is analyzed by ICP-MS. The remaining residue of the ammonium acetate extractions is then stirred with 1 molar hydrochloric acid (HCl) at 70 °C for 24 h to remove the elements held in coordination complexes (chelates) within the organic structure of the coal, as well as acid-soluble minerals such as carbonates, some oxides, and sulfates. The hydrochloric acid extraction is repeated once. The residue is then analyzed by ICP-MS. The elements remaining in the sample after the extractions are determined by difference. The nonextractable elements are associated in the sample as silicates, aluminosilicates, sulfides, and insoluble oxides.

5 Rare Earth Elements Abundance and Distribution Trends

Sections 5.1 and 5.2 provide the results of sample characterization for the Hagel Beds at Falkirk Mine as well as the Harmon-Hanson outcropping samples. The abundance and distribution (i.e., ratio of HREE to LREE or normalized to crustal averages) of the REE in the samples are presented and discussed.

5.1 Falkirk Mine—Hagel Beds. The total REE content (ash basis) for samples from the Falkirk Mine is presented as Fig. 2 for the stratigraphic column at multiple locations in the mine. The samples represent at least one-foot thick layers within the column. The data show that the associated sediments are typically less than 200 ppm, but that in certain locations within each of the coal seams sampled, there are spikes of higher REE content. However, the REE content in the coals was not uniform along the column. For example, only one location in Hagel A exhibited high REE content at approximately the middle of the seam, which happens to be just below a clay parting. Overall, the Hagel B coal had the most uniform distribution of high REE content. The samples collected from Coal Creek Station had relatively low total REE content, which was due to the bulk mining practices at Falkirk that involve mixing of multiple seams as well as clay materials, which dilutes the REE content in the run-of-mine coal fed to the

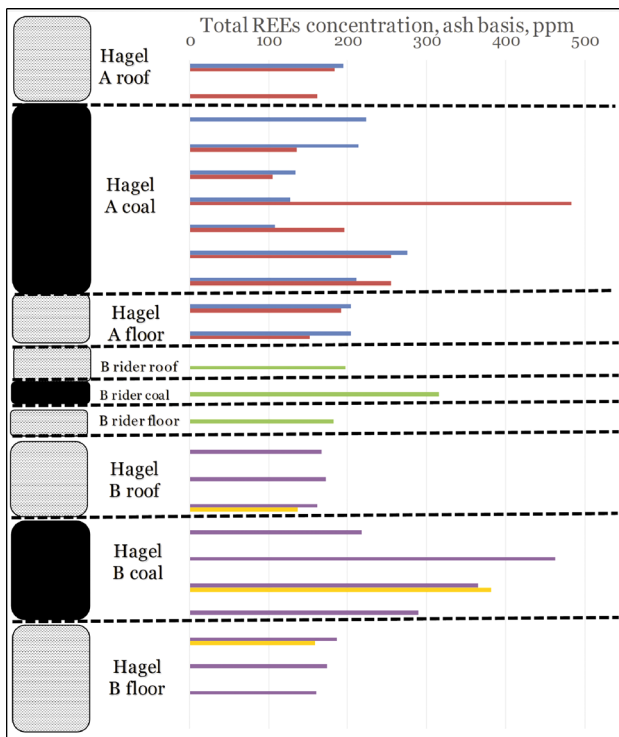


Fig. 2 Rare earth elements content in the Falkirk Mine stratigraphic column (ash basis)

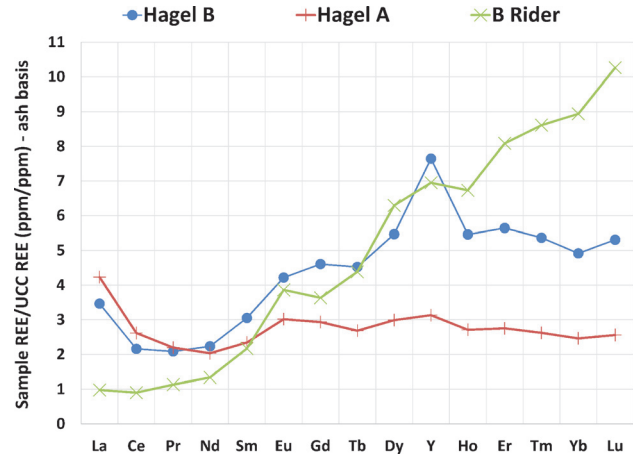


Fig. 3 Upper continental crust-normalized REE distributions for selected Falkirk Mine lignite coal samples (ash basis)

plant. At the Coal Creek Station, the REE content in the mineral-rich reject stream from the DryFining process was depleted in REE compared to the cleaned coal stream on an ash basis, indicating that the REE are not associated with the heavy mineral fraction in the coal. Overall, the highest REE content at the plant was the fly ash and bottom ash samples, at about 240 ppm and 270 ppm, respectively, on an ash basis. In comparison, the reject stream was about 120 ppm on an ash basis.

Selected coal samples from each of the seams sampled at Falkirk Mine (Hagel A, B Rider, Hagel B) have been normalized to the upper continental crust (UCC) REE concentrations and plotted against molecular weight to see the shape of the REE distribution, as shown in Fig. 3. Seredin and Dai previously described light (L-type), medium (M-type) and heavy (H-type) distributions using this approach [12]. The data show that the Hagel A sample has an M-Type distribution, while the Hagel B and B Rider have H-type distributions, with the B-Rider being more strongly H-type. The Hagel B sample has a strong positive Y anomaly.

This same type of analysis method has been plotted in Fig. 4 for selected roof/floor samples from Falkirk Mine. Samples were selected from roof and floor sediments for each of the major stratigraphic sections sampled in the mine and represent approximately one-foot thick layers immediately above and below the main coal seams. Overall, the data show an M-type distribution, with strong positive anomalies centered on Eu, as well as Ce-minima and pronounced Y-minima. However, interestingly, in each case, the roof sediments for the stratigraphic sections are depleted in the HREE compared to the floor sediments. Additionally, with the exception of the B Rider sediments (very close distributions), the LREE are enriched in the roof materials compared to the floor materials. Combined, these data suggest accumulation of REE in the coal resulted from preferential leaching of the HREE from the clays and subsequent adsorption into the coal/organic matter, an assertion that is substantiated by the enrichment in the coal for these particular elements. Further, the B Rider sediments show the overall highest enrichment in the HREE, which is consistent with the observation of enrichment in these elements in the B Rider coal seam (Fig. 3).

5.2 Harmon-Hanson. Table 2 summarizes abundance of REE in selected samples from the Harmon-Hanson coal zone and other locations in southwestern North Dakota collected during several sampling trips by the North Dakota Geological Survey. The sample nomenclature shown in the table is the same as used by Kruger et al. [25]. However, the REE analyses were conducted independent of the NDGS efforts, and thus the total REE values may not be identical. The range of REE abundance in the samples varied from 47 to over 600 ppm on a dry whole sample basis and

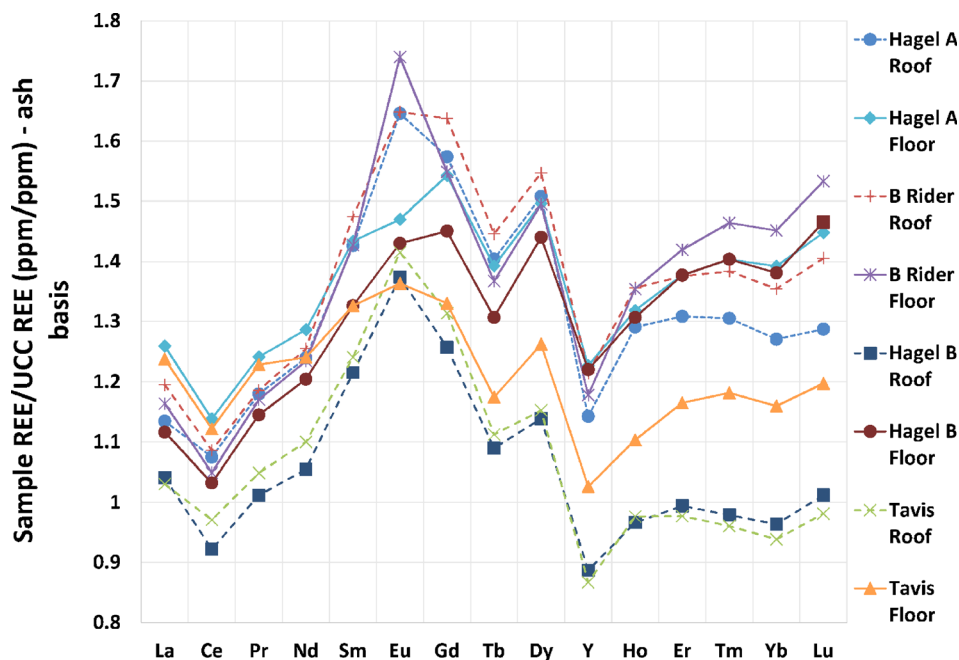


Fig. 4 Upper continental crust-normalized REE distributions for selected Falkirk Mine roof/floor sediments (ash basis)

Table 2 Rare earth elements in Harmon-Hanson coal zone samples

NDGS report sample ID [25]	Ash yield (dry, wt %)	Total REE, ppm (dry coal basis)	HREE/LREE	Total critical REE, ppm	Total REE, ppm (ash basis)
55 ^a	36.3	642	0.28	191	1752
54A	20.1	564	0.35	189	2235
55-2	75.5	449	0.28	129	587
5A	40.5	363	0.89	151	892
21C	60.9	322	0.43	104	525
2AA	47.0	212	2.06	94	449
34F	20.9	194	0.76	83	924
23G	32.2	177	0.45	54	541
29O	26.2	146	0.69	61	554
4F	15.9	105	0.84	42	659
34E	11.0	76	2.19	42	681
3H	15.7	76	1.00	34	480
4E	10.2	47	1.30	21	462

^aThis sample collected near sample 55-2 in the same seam, but not detailed in the NDGS report.

as high as 2200 ppm on an ash basis, and represents both coals (i.e., < 50% ash) and clay-rich sediments collected from the margins of the coal seams and in the associated roof/floor/partings materials. Overall, the REE abundance in these samples is significantly higher than the Hagel Bed samples from Falkirk Mine. Six of the sampling locations exceeded 200 ppm TREE (dry whole sample basis), with four of these being coals (<50% ash content) and the other two being clay-rich sediments. The 2AA and 5A samples are particularly interesting from the standpoint of their extreme enrichment in the more valuable and less common HREE. The 3A sample had the highest content of Dy-Lu and Y of all samples collected in this study, while the 6AA sample has a very high HREE/LREE ratio of greater than two. Some of the very low ash coal samples (34E, 3H, and 4E) also have attractive ratios of HREE/LREE.

Figure 5 displays the UCC-normalized REE distribution for selected Harmon-Hanson coals. Overall, the distribution of REE shows strong enrichment of the middle and heavy weight REE compared to the UCC. The 54A and 55 samples (collected from the same seam in different stratigraphic layers) are more enriched

in the middle weight REE, while the 5A and 2AA samples are more enriched in the heavy weight REE.

6 Rare Earth Elements Forms and Modes of Occurrence

The modes of occurrence of the REE in the associated sediments were determined by SEM methods. Only La, Ce, and Y were detected in any of the SEM-EDS measurements. However, the REE-bearing minerals appear to be zirconium minerals, aluminophosphates (i.e., crandallite), and clays. CCSEM analysis identified many of the same REE-elemental associations as the SEM-EDS measurements. However, the CCSEM also determines the size of REE-bearing minerals/grains in the samples. In the associated sediments, the REE are associated in ultra-fine mineral grains of less than 4 μm in diameter. For the coal samples, SEM methods proved ineffective in locating REE-bearing minerals. Unlike higher rank coals (bituminous, anthracite), lignite coals contain oxygen that is in the form of oxygen functional groups such as carboxylic acids. These groups provide sites for bonding

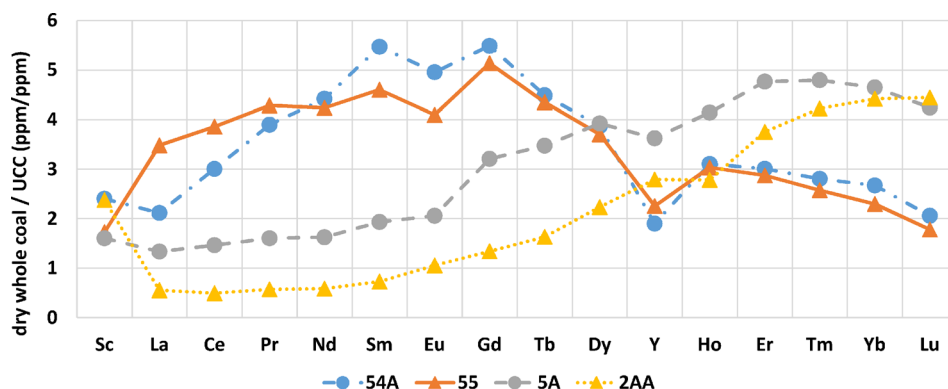


Fig. 5 Upper continental crust-normalized REE distributions for selected Harmon-Hanson lignite coal samples (dry coal basis)

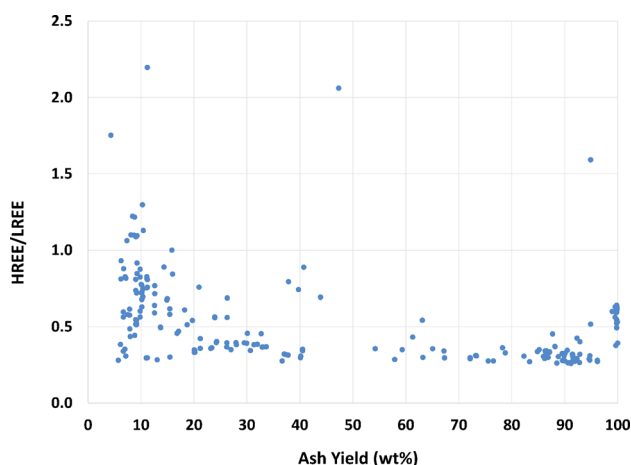


Fig. 6 Ratio of heavy to LREE for all samples as a function of sample ash content

of cations to the organic matrix in the coal on ion exchange sites and coordination complexes [29]. As a result, significant quantity of certain elements (including REE) can be organically associated in lignite coals, rather than found in hard mineral associations, making them essentially invisible to SEM techniques. Thus, other methods of determining modes of REE occurrence in the coal samples were employed, as discussed subsequently.

Based on the ICP-MS results of all North Dakota lignite and sediment samples analyzed in this study, correlations have been prepared that relate the ash content of the samples and parameters that describe the distribution of the individual REE within the total sample. Figure 6 shows all of the data obtained, with the ratio of HREE/LREE plotted against ash content of the sample. The data clearly show that the ratio increases in the low ash samples (i.e., the coal samples), suggesting higher organic affinity of the HREE.

Using a similar approach, the individual REE have been broken out in light (La, Ce, Pr, Nd, Sm), medium (Eu, Gd, Tb, Dy, Y), and heavy (Ho, Er, Tm, Yb, Lu) molecular weights and the total REE (ash basis) in each group have been normalized to UCC averages and have been plotted against ash content of the sample, as shown in Fig. 7. Here, the data clearly show that the medium and heavy REE have higher enrichment in low ash materials, as compared to the lights, whereas in the high-ash samples, the data show a similar distribution to earth's crust (i.e., Y -axis value of about 1.0). This also provides evidence of the heavier REE having a higher affinity to the organic coal fraction.

To further examine the organic versus mineral association of the REE, float-sink analysis was conducted. The results for a high

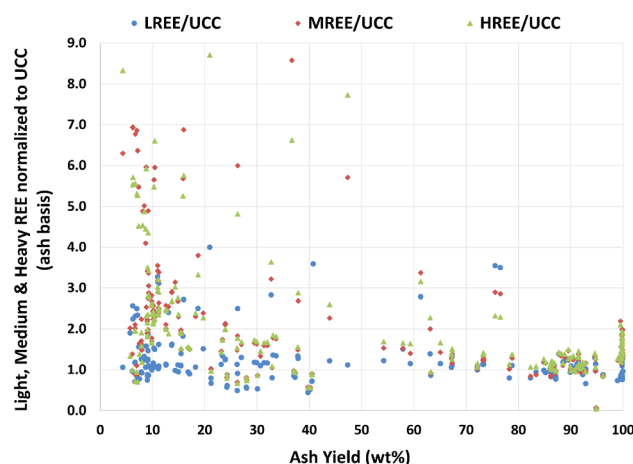


Fig. 7 Upper continental crust-normalized light (LREE), middle (MREE), and heavy (HREE) molecular weight REE for all samples (ash basis)

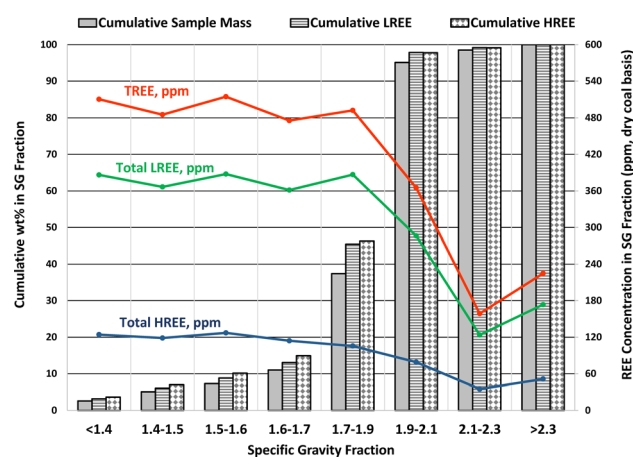


Fig. 8 Float-sink density separation analysis. REE concentration and weight distribution as a function of specific gravity (dry coal basis). Harmon-Hanson sample 55-2.

ash Harmon-Hanson sample (55-2), shown in Fig. 8, indicate that the mineral-rich fractions (higher specific gravity fractions) are depleted in REE and that the organic-rich fractions are enriched in REE by a factor of about 2.5 on a dry whole sample basis. This is a further indication of the organic association of the REE.

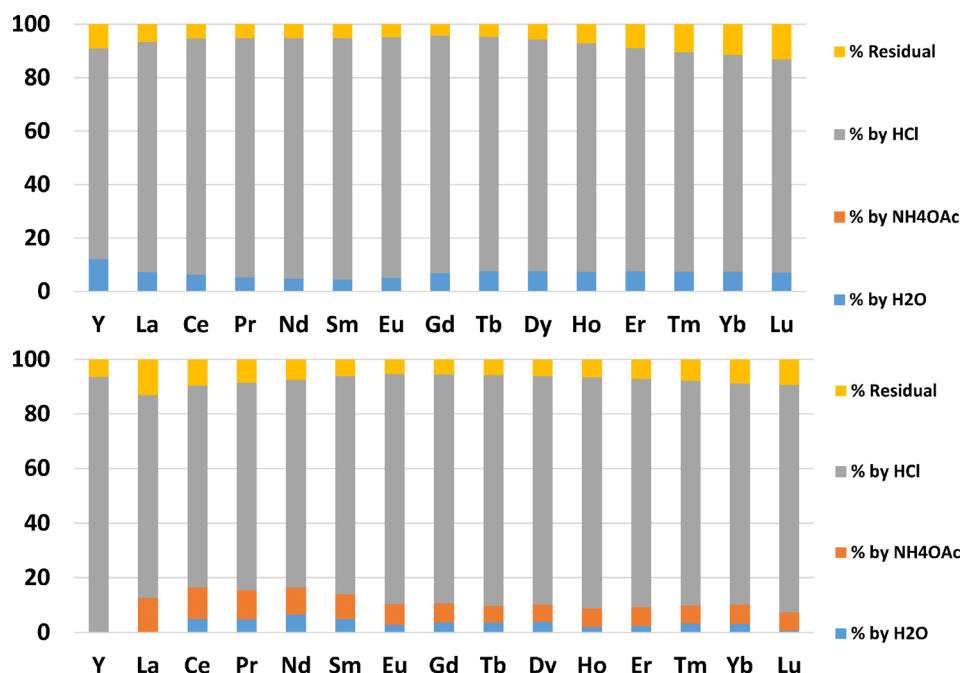


Fig. 9 Results of chemical fractionation tests for two North Dakota lignite coals. Top—Harmon-Hanson 54A; Bottom—Hagel B.

There are several examples in the literature that validate this inferred evidence of organic REE associations in coal. Seredin and Dai [12] have compiled a review of the various forms of organic REE associations in coals [12]. Many REE-rich coals can contain a significant proportion of their total REE as organically associated, particularly in coal with low ash and low-rank (lignite, subbituminous). A number of inferred organic associations have been observed by methods such as negative correlation of REE content with ash yield and enrichment of REE in the light-specific gravity fractions [30–37]. These types of indirect methods are validated by experimental work evaluating the sorption characteristics of REE by peat, coals, and humic acids [38,39]. Further evidence of organic associations can be inferred by the presence of mainly LREE-bearing minerals in coals that also exhibit M-type or H-type REE distributions, suggesting that the medium and heavy REE are enriched in the organic matter. Direct evidence of organic associations is also available in the literature. For example, Seredin and Shpirt [40] have shown that about 50% of the REE content of two Russian coals were contained within the humic matter, and were easily extracted by dilute caustic leaching. Their testing also showed that the humic matter is slightly enriched in the medium weight REE, compared to the light and heavy REE. Sequential extraction methods have also been used to determine REE modes of occurrence. For example, Finkelman et al. [41] evaluated three low-rank coals, including a North Dakota lignite, and a series of higher rank coals and discovered that the extraction behavior of the REE and some other trace elements were significantly different in the low-rank coals. They attributed the much higher extraction of the REE in the low-rank coals to their likely association in organic coordination complexes, whereas the higher rank coals appeared to contain mainly mineral REE forms. In a similar sequential acid leaching approach, Wei and Rimmer [42] reached a similar conclusion that many trace metals, including REE, in two Chinese low-rank coals were weakly bound in chelate groups within the organic matter of the coals. Eskenazy [38] found that Na^+ , K^+ , Ca^{2+} , and Mg^{2+} bound to $-\text{COOH}$ and $-\text{OH}$ were replaced by REE cations. Aude [43] showed that HREE–organic complexes are more stable than LREE–organic complexes, and that a decrease in pH causes a decrease in the stability of the complexes [44,45]. Finkelman also

found that the HREE preferentially complexed over the LREE with the organic matter [46]. Loosely bound REE can also be found adsorbed to clay matter within the organic matrix or onto the humic matter [34,47].

To quantitatively validate this study's inferred evidence of organic REE associations in the lignite coals, chemical fractionation, a sequential leaching process was used. Results of the chemical fractionation tests for two ND lignites (Hagel B, Harmon-Hanson 54A) are provided in Fig. 9. Several additional coals were evaluated in this study using this method, and results were quite consistent, with the majority of the REE extracted by HCl, indicating their presence as organic complexes, or in acid soluble minerals such as carbonates, sulfates, and some oxides. There was some water-soluble or ion-exchangeable REE (extracted by NH_4OAc) in each of the samples as well. Overall, these results show that about 80–95% of the REE in ND lignite coal are extractable through the HCl leaching step. The remaining REE (% residual) would be associated in non-HCl-soluble minerals, such as clays, silicates, sulfides, or others. These data validate the inferred evidence of organic associations and are consistent with literature.

7 Summary and Conclusions

Sampling was conducted on a range of North Dakota lignite and lignite-related materials. Characterization determined the content of REE, the distribution of the specific REE, and the modes of occurrence of the REE in the various samples. In the Falkirk Mine, the associated sediments had the highest REE content on a whole sample basis, and typically ranged from about 150–200 ppm. However, on an ash basis, for each of the coal seams evaluated (Hagel A, B Rider, Hagel B), specific locations within the coal seams showed significantly higher REE content, ranging from about 300–600 ppm, with the Hagel B exhibiting the highest content and most uniform distribution over the sampling area. At Falkirk Mine, the roof sediments are depleted in the HREE and enriched in the LREE compared both to the coal seams and floor sediments below, suggesting preferential leaching of the HREE from the clays with accumulation in the coals.

The content of REE was found to be variable along the stratigraphic column at Falkirk Mine. However, REE content appears to be more uniform on lateral planes. For REE recovery to be feasible, “selective” mining practices to target specific layers within the seams with highest REE content are likely needed. In the Coal Creek Station, overall REE content was relatively low. This is caused by the blending practices at the Falkirk mine, which results in dilution of high REE content coal with coals of lower REE content.

Samples collected from the Harmon-Hanson coal zone in southwestern North Dakota showed by far the highest REE concentration, with coals exceeding 600 ppm on a dry coal basis or 2000 ppm on an ash basis. This is in comparison to the best coal from the Falkirk Mine (Hagel B), which was about 50 ppm on a dry coal basis or about 580 ppm on an ash basis. The clay-rich sediments from the Harmon-Hanson samples were also significantly more enriched in the REE compared to the sediments from Falkirk Mine. Samples both from the Falkirk Mine and the Harmon-Hanson coal zone exhibited strong enrichment of the middle and heavy molecular weight REE, with some samples having HREE/LREE ratios exceeding two.

The clay-rich sediments associated with the coal seams had REE mainly associated in mineral grains of less than four microns in diameter, in zircon minerals, aluminophosphates, and clays. Inferred evidence of organic association of REE in North Dakota lignite coal was revealed by correlating the enrichment by molecular weight of the REE with the ash content of the sample, as well as by float-sink analysis that showed significantly higher concentration of REE was present in the low specific gravity organic-rich fractions of a high-ash sample from the Harmon-Hanson coal zone. Experimental evidence of organic associations was gathered via chemical fractionation tests, which showed that REE in the lignite coals are primarily associated in organic coordination complexes, and to a lesser extent as ion-exchangeable cations or water soluble minerals. A small fraction (5–20%) is associated with silicates, clays, sulfides, or other non-HCl-soluble minerals. The chemical fractionation data, combined with inferred evidence and literature, indicate that the REE in North Dakota lignites appear to be primarily associated with the organic matrix.

Combined, the data suggest that an infiltrational process of accumulation of REE in the coals has occurred in North Dakota. During the process of the accumulation of organic material that formed lignite coal, the coal forming materials interacted with detrital materials such as volcanic ash that contain rare earth elements. Combined with surface water leaching processes, the resulting interaction caused the REE to be released from the detrital material into the anaerobic swampy environment. The REE in solution were able to react with abundant oxygen functional groups and become associated with the organic matrix during compaction and coalification. This high percentage of organically associated REE is unique to low rank coals such as lignite and subbituminous coals. This is due to the “age” of the low-rank coals, where significant secondary mineralization has yet to occur, and thus the adsorbed REE remain bound with the oxygen functional groups in the coal, rather than in mineral forms typically found in older/higher rank coals.

Overall, this study has laid the groundwork for additional feasibility assessment of rare earth element recovery from North Dakota lignite coal and lignite-related feedstocks. The abundance of REE has shown to be elevated in multiple locations and sample types, and the forms and modes of occurrence of the REE in the samples have been determined that will inform the development of extraction methods to recover and concentrate the REE. This study has revealed that North Dakota lignite coal and related materials are a promising alternative resource for REE recovery.

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Nomenclature

CCSEM	= computer controlled scanning electron microscopy
Coutl	= outlook coefficient
HREE	= heavy rare earth elements
ICP-MS	= inductively coupled mass plasma mass spectrometry
LREE	= light rare earth elements
MW _e	= megawatt electric
NDGS	= North Dakota Geological Survey
NH ₄ OAc	= ammonium acetate
PC	= pulverized coal
ppm	= parts per million
REE	= rare earth elements
REYdef,rel%	= percentage critical rare earth elements in total sample
SEM-EDS	= scanning electron microscopy energy dispersive X-ray spectrometry
TREE	= total rare earth elements
UCC	= upper continental crust

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