

Rare Earths in Coal

Ned W. Kruger

Introduction

Market demands continue to grow for rare earth elements, or metals, used by the industries responsible for many of the modern conveniences and high-technological advances of the past several decades. These metals are found inside many of the electronics and energy efficient items found in the typical American home or business such as computers, cell phones, televisions, and LED and CFL light bulbs. Is there an electric or hybrid vehicle in your garage? It has roughly 2-3 pounds of neodymium, terbium, and dysprosium in the magnets of its motor and 20-30 pounds of lanthanum in its battery (Gorman, 2009). Some rare earths are crucial components for the super-power permanent magnets used in industrial generators, which transform alternative forms of energy such as wind, tidal, and geothermal into electricity (Seredin and others, 2013). Health care applications include the use of rare earths as catalysts by biomedical and chemical researchers; use in imaging (CAT scans, MRIs, PET, and X-ray) by way of their optical and magnetic properties; and use in a variety of laser treatments including those for skin cancer (neodymium), non-invasive procedures for cancers and kidney stones (holmium), and tattoo removal (yttrium, erbium, and thulium) (RETA, 2016). An exhaustive list of rare earth applications is not the intent herein; however, other rare earth-containing products which merit inclusion are superconducting electric power lines, semi-conductors, and lightweight aerospace components. A 2014 report by the American Chemistry Council stated over \$329 billion of economic output and 618,000 jobs in North America are supported by rare earth chemistry (Rozelle and others, 2016). For additional information on rare earth elements please see Kruger, 2015.

Maintaining reliable sources of rare earth-containing raw materials, the vast majority of which are currently produced in China, is critical to each of the industries and manufactured products mentioned above. New sources must be identified and developed to ensure an adequate supply of these important metals is available today and for the technological advances of the future. Recent publications indicate the potential of coal deposits for the recovery of rare earths as by-products of mining and combustion (Seredin and Dai, 2012; Seredin and others, 2013; Franus and others, 2015). In particular, lignite has been highlighted owing to its potential for higher concentrations of rare earths and because there are existing techniques for extracting rare earth metals from the low-ranking coal (Seredin and Dai, 2012).

The North Dakota Geological Survey is in the process of acquiring data on the quantity of rare earth elements present in the lignite beds and adjacent materials via sample collection from their exposures in the badlands region of

southwest North Dakota. Goals of the program are to identify coal seams in which rare earths are concentrated beyond that found in average coal deposits, identify positions within a coal body where rare earths are most apt to be concentrated, and to spot trends in the data that may signal condition sets under which enrichment of rare earths is more likely to have occurred. Approximately 275 samples have been collected from 26 locations throughout Billings, north-central Slope, eastern Golden Valley, and southern McKenzie Counties (fig. 1). To date, 100 of these samples representing 12 sample locations have been analyzed. Statistics prepared from these analyses are presented in table 1. The lignite beds found at and near the surface in this region were deposited 55-60 million years ago along with claystone, siltstone,

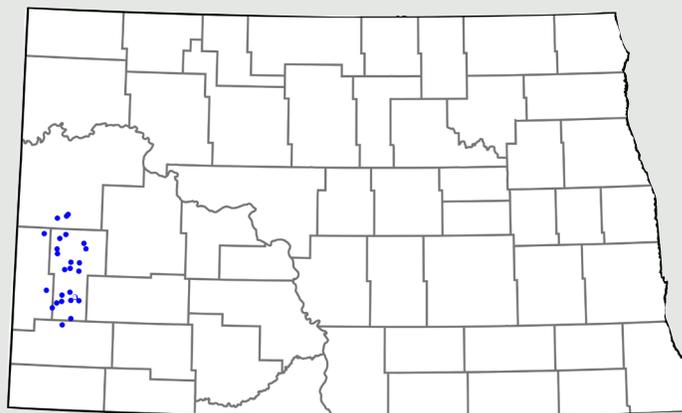
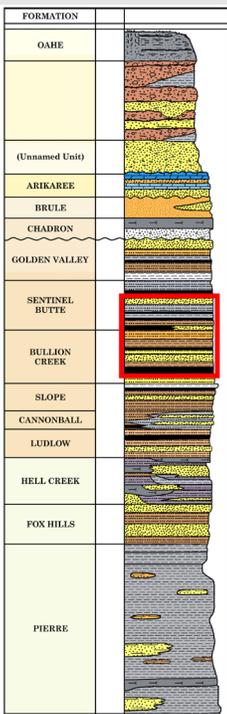


Figure 1. County map of North Dakota. The blue dots represent the 26 locations from which samples for rare earth elements have been collected. Sample localities are scattered throughout Billings, north-central Slope, eastern Golden Valley, and southern McKenzie counties.

Table 1. General statistical breakdowns for each individual rare earth element reported from the 100 samples analyzed. UCC = upper continental crust.

Element	Concentration in parts per million				Total REE % samples	Total REE % UCC
	Low	High	Average	Median		
Cerium	3.1	206	26.8	13.6	29.8	38.0
Dysprosium	0.4	17.9	3.2	2.1	3.5	2.1
Erbium	0.18	11.4	2	1.47	2.2	1.4
Europium	0.07	7.55	0.8	0.43	0.8	0.5
Gadolinium	0.3	26.1	3.2	1.9	3.5	2.3
Holmium	0.07	3.75	0.7	0.495	0.7	0.5
Lanthanum	1.6	72.9	12.9	7.5	14.4	17.8
Lutetium	0.02	1.67	0.3	0.24	0.3	0.2
Neodymium	1.9	136	13.6	6.9	15.2	15.4
Praseodymium	0.4	30.3	3.4	1.7	3.7	4.2
Samarium	0.3	32.9	3.1	1.6	3.4	2.7
Terbium	0.06	3.66	0.5	0.33	0.6	0.4
Thulium	0.02	1.64	0.3	0.23	0.3	0.2
Ytterbium	0.14	10.5	1.9	1.43	2.1	1.3
Yttrium	2	91	17.4	14	19.3	13.1
Total REE	15	603	90	51	100	100



and sandstones of the Bullion Creek and Sentinel Butte Formations (fig. 2). Sediments were transported into the study area by river systems emanating from the west and northwest. The Bullion Creek Formation contains greater amounts of fine-grained material and shows greater development of thicker, more widespread coals compared to the Sentinel Butte Formation (Murphy, 2006). Volcanism associated with tectonic activity is believed to have been more prevalent during the deposition of the Sentinel Butte Formation (Royce,

Figure 2. North Dakota stratigraphic column (modified from Murphy et al., 2009). Coal beds exposed at the surface within the sampling area belong to the Bullion Creek and Sentinel Butte Formations, and are outlined in red.

1970), which may increase the likelihood of observing remnant deposits of volcanic ash falls, or tonsteins, within the coals deposits of the Sentinel Butte Formation.

Analytical results thus far have identified samples in which the total rare earth content was significantly higher than average content estimates of 68.5 parts per million for world coal and 62.1 parts per million for USA coal (Seredin and Dai, 2012). These areas of enriched concentrations have primarily been identified in coal beds less than 2 feet thick, or when identified within thicker beds are typically located at the coal roof or floor or adjacent to clay partings. A majority of samples with average and above rare earth content also show desirable ratios of critical rare earth elements compared to those which are currently produced at a volume which exceeds their demand. The average percentages of total rare earths calculated for europium, dysprosium, erbium, terbium, and yttrium, each considered critical in economic class, display enrichment compared to the broad averages of all materials from the upper continental crust (table 1). It has been observed that coals overlain by sandstone (fig. 3) and coal stringers within sandstone also show overall rare earth enrichment, although this



Figure 3. Two coal beds (1 and 2) separated by eight feet of claystone containing iron-oxide nodules. The upper coal (#1) is overlain by a thick sandstone. Photo taken in McKenzie County.

is based on a very limited number of samples. We are waiting to see whether further analytical results of sample material collected from similar host locations support this observation.

It is hoped that additional sampling and analyses may lead to a greater understanding of the effect of fine-grained over- and under-burden, clay partings, tonsteins, and carbonaceous shales on rare earth content (fig. 4). Data is being evaluated for rare earth characteristic commonalities and differences between the two host formations. The NDGS is also collecting samples of coal-ash where the coals have burned in-place to evaluate the extent to which this process may naturally concentrate metals and whether coal-ash at the base of clinker deposits could support a mining operation with rare earths as the primary resource.

References

Franus, W., Wiatros-Motyka, M.M., and Wdowin, W., 2015, Coal fly ash as a resource for rare earth elements: *Environmental Science and Pollution Research*, v. 22, p. 9464-9474.

Gorman, S., 2009, <http://www.reuters.com/article/us-mining-toyota-iodUSTRE57U02B20090831>, (retrieved November 2, 2016)

Kruger, N.W., 2015, A "Rare" Opportunity: *Geo News*, v. 42, no. 1, p.7-9.

Murphy, E.C., 2006, The lignite reserves of North Dakota: North Dakota Geological Survey, Geologic Investigations No. 104.

Murphy, E.C., Nordeng, S.H., Juenker, B.J., and Hoganson, J.W., 2009, North Dakota stratigraphic column: North Dakota Geological Survey, Miscellaneous Series No. 91.

RETA, 2016, <http://rareearthtechnicalalliance/Applications/Health-Care.html> (retrieved Nov. 2, 2016)

Royce, C.F., 1970, A sedimentologic analysis of the Tongue River-Sentinel Butte interval (Paleocene) of the Williston Basin, western North Dakota: *Sedimentary Geology*, v. 4, p. 19-80.

Rozelle, P.L., Khadilker, A.B., Pulati, N.S., Klima, M.S., Mosser, M.M., Miller, C.E., and Pisupati, S.V., 2016, A study on removal of rare earth elements from US coal byproducts by ion exchange: *Metallurgical and Materials Transactions E*, published online Jan. 4, 2016.

Seredin, V.V., and Dai, S., 2012, Coal deposits as potential alternative sources for lanthanides and yttrium: *International Journal of Coal Geology*, v. 94, p. 67-93.

Seredin, V.V., Dai, S., Sun, Y., and Chekryzhov, I.Y., 2013, Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies: *Applied Geochemistry*, v. 31, p. 1-11.



Figure 4. A half dozen coals are exposed at this outcrop along the little Missouri River in Billings County. Two of the six coals are overlain by channel sandstones.