Estimating Rare Earth Concentrations

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Introduction

The North Dakota Geological Survey (NDGS) remains busy sampling lignite coal (fig. 1) and related rock materials for rare earth elements (the lanthanides plus yttrium and scandium). The program, which began in the summer of 2015 (Kruger, 2015, 2017), has identified lignite and carbonaceous clays enriched in rare earth elements and expanded its scope to include other critical elements in 2018 (see the related article by Levi Moxness in this issue). Now in our sixth field season, the NDGS has collected over 1,400 lignite and other rock samples, produced two reports of investigation (Kruger et al., 2017; Murphy et al., 2018) and continues to grow our database, consisting of analyses from more than 950 samples, a majority of which include a full suite of rare earth elements. Having such an extensive database of analyses provides the opportunity to learn more about the degree and consistency to which one rare earth element corresponds to the others.

Figure 1. Survey geologists Levi Moxness (left) and Ned Kruger (right) use a battery-operated drill fitted with a soil auger bit to collect a coal sample in Slope County.

The estimates

Elemental concentration correlations between individual elements and between an element and the total rare earth concentration can be visualized in graphs generated in a spreadsheet application. Beginning with a spreadsheet containing a full suite of rare earth analyses from 828 samples, scatter plots similar to those shown in fig. 2 were graphed for each of the sixteen elements compared to the total rare earth concentration. The resultant graphs showed all the rare earth elements correlate to the total rare earth concentration to various degrees. Generally, the correlations to

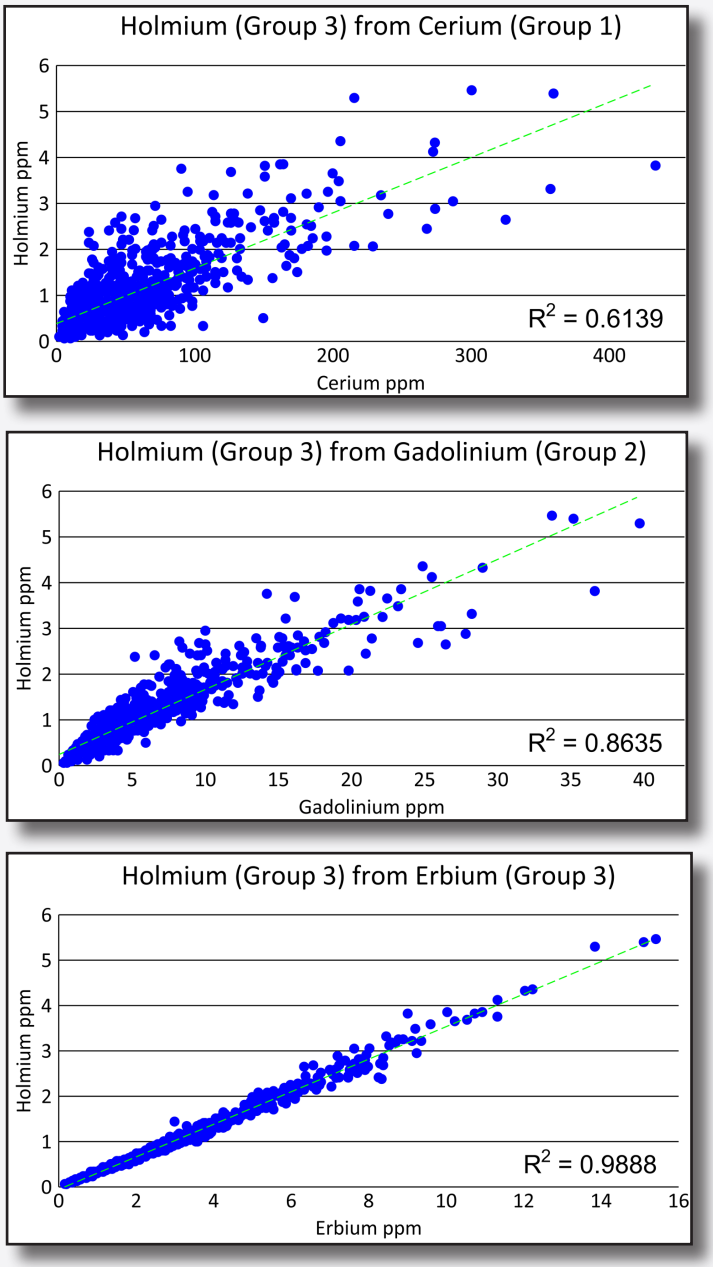

Figure 2. Three graphs showing the laboratory reported concentrations for holmium (group 3) compared to those of cerium (group 1), gadolinium (group 2), and erbium (group 3), each with a trendline and coefficient of determination value (R^2). R^2 values are a measure on a scale of 0 to 1 (low to high) of the degree to which a variable on the y-axis can be calculated by multiplying a second variable (x-axis) by the slope of the trendline.

total rare earth concentrations were observed to be strongest in the lightest lanthanides and weakened as you progress through the heavier lanthanides. Three basic patterns were identified in the elemental scatter plots and the elements were sorted into groups accordingly (table 1a).

Element to element correlations are strongest when comparing elements within the same group. The points of a scatter plot comparing two elements in the same group tend to cluster along its trendline. Although a scatter plot comparing two elements from different groups shows some degree of correlation, the point plots fall farther from the trendline and the accuracy of determining one element concentration (y) from the slope of the trendline and a known concentration of the other element (x) is diminished (fig. 2).

Lanthanum, cerium, neodymium, gadolinium, erbium, yttrium, and scandium were chosen as the initial seven elements for which the laboratory-measured concentrations would be used. They were selected based on their overall prevalence (table 1a), affiliations with the other rare earths, and economic rank. Concentrations for the other nine elements were calculated by linear regressions based on the trendlines of each element compared to its closest affiliated element(s) with a lab concentration. A total rare earth concentration estimate was then calculated for each sample as the sum of all element concentrations. The process was repeated, removing one known lab concentration at a time, to evaluate accuracies based on as few as two elements. The laboratory concentration for scandium was used in all estimate scenarios because of its high economic importance and because it shares the least predictive correlations to the other rare earth elements.

Table 1a. Information on the individual rare earth elements, including the average deviation of estimates from laboratory measurements.

	Element	Atomic Number	Percent of total REE in database samples	Average deviation of each element's estimate from actual concentration (±%)					
				7 Element	6 Element	5 Element	4 Element	3 Element	2 Element
Group I	Lanthanum	57	13.9	*	*	*	12.4	12.4	12.4
	Cerium	58	30.8	*	*	*	*	*	*
	Praseodymium	59	3.8	3.6	3.6	3.6	3.6	7.3	7.3
	Neodymium	60	15.4	*	*	*	*	12.3	12.3
Group II	Samarium	62	3.3	16.1	16.1	16.2	16.2	20.8	26.7
	Euporium	63	0.8	13.3	13.3	22.7	22.7	25.1	34.0
	Gadolinium	64	3.3	*	*	17.2	17.2	19.1	27.9
	Terbium	65	0.5	10.0	10.0	21.4	21.4	24.6	36.9
	Dysprosium	66	3.0	7.4	8.1	17.9	17.9	18.5	36.1
Group III	Holmium	67	0.6	6.2	11.8	11.8	11.8	11.8	43.4
	Erbium	68	1.7	*	9.8	9.8	9.8	9.8	43.7
	Thulium	69	0.2	6.4	12.5	12.5	12.5	12.5	47.0
	Ytterbium	70	1.5	9.0	14.0	14.0	14.0	14.0	45.0
	Lutetium	71	0.2	13.7	19.2	19.2	19.2	19.2	49.2
	Yttrium	39	15.0	*	*	*	*	*	46.8
	Scandium	21	5.9	*	*	*	*	*	*

* Laboratory concentration was used in the estimate

Table 1b. Estimate information for total rare earth concentration compared to the actual laboratory information.

Total Rare Earths	Estimate					
	7 Element	6 Element	5 Element	4 Element	3 Element	2 Element
Approximate fraction of unknown elements	14%	16%	19%	33%	48%	63%
Range of the estimate deviations from lab totals	-2.6 to 1.8%	-4.2 to 4.8%	-8.6 to 6.1%	-10.3 to 5.7%	-19.4 to 13.7%	-56.4 to 65.4%
Average deviation	±0.37%	±0.89%	±1.85%	±1.62%	±2.77%	±12.2%

The seven-element estimate for total rare earth concentrations was shown to be quite accurate, deviating from the laboratory measurements in a range of -2.6 to 1.8 percent (table 1b). In each estimate scenario, estimates for individual elements (table 1a) deviated by a wider range than that of the total rare earth concentration.

The estimates' predictive abilities at higher concentrations than the initial dataset were tested. The first batch of samples analyzed for only seven elemental concentrations included a sample for which the total rare earth estimate was calculated to be 1,599 parts per million (ppm), approximately 40 percent higher than our highest reported concentration at the time. Intrigued by this number, and quite honestly wishing to round it out with just one more ppm, and given a chance to verify estimates at higher concentrations than had previously been available, laboratory-measured concentrations for the other nine rare earth elements of this sample and several others were requested. The results were verified (fig. 3). The lab reported total rare earth concentration was 1,598 ppm. This estimate was within six-hundredths of one percent of the laboratory's measurement, a very precise estimate by nearly any standard. This concentration is now believed to be the highest concentration of total rare earths reported in a North American coal.

The data generated from these estimate models show that analytical costs can be reduced by selectively choosing only a partial set of rare earth elements for analysis, depending on your situational accuracy requirements. The savings can be applied toward collecting more data points to better characterize a study area (Kruger, 2020). The estimate formulas may also be accurate for coals and other sedimentary rock types found in North Dakota or elsewhere.

References

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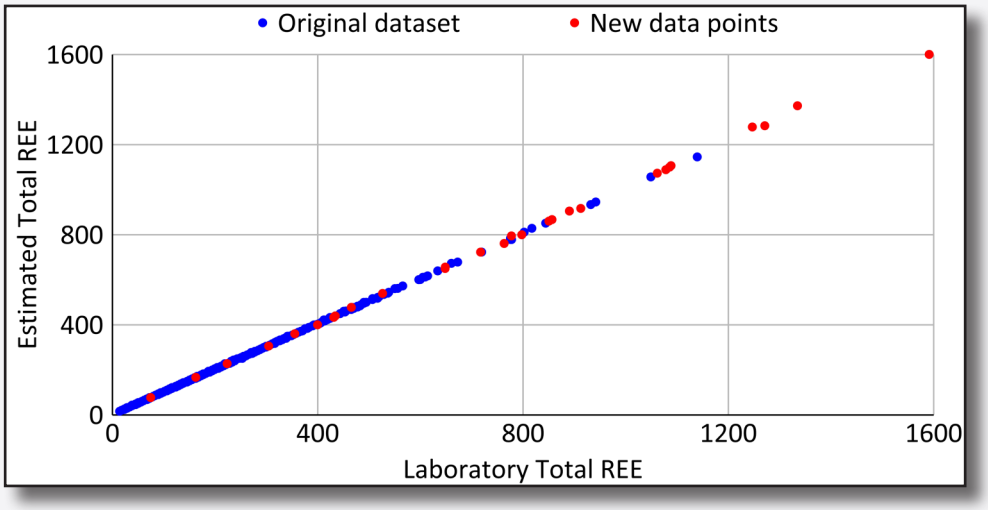

Figure 3. A graph showing the plots of the total rare earth concentrations based on the seven-element estimates (y-axis) compared to the laboratory reported concentration (x-axis) for each sample in the original dataset (blue) and new data points (orange). The resulting plot shows a very strong ability to accurately estimate the total rare earth concentration of a sample from the laboratory reports of just seven of the rare earth elements.