Development of Predictive Tools to Identify Critical Mineral Enrichment in High-Alumina Underclays of the Appalachian and Illinois Basins, USA

Bethany Royce, Gary Daft, Philip Dinterman, and Jessica Moore, West Virginia Geological & Economic Survey

Sarah Brown, LRST National Energy Technology Laboratory, MGN

Abstract

The USGS Earth Mapping Resources Initiative (Earth MRI) works to identify mineralized areas or deposits across the United States that may host critical minerals. Aluminum-rich clays associated with coal horizons have the potential to be low-grade, large-volume, critical mineral resources. Past studies show that alumina is routinely 20-40% in these clay layers, and preliminary geochemical data indicate that some clay layers host anomalously high (>300 ppm) rare earth element (REE) concentrations. However, understanding of the distribution of metals in varying lithologies and stratigraphic positions is limited by data density and a lack of modern geochemical data. Ongoing work through Earth MRI includes geochemical analyses, mapping of known deposits, and determination of the stratigraphic and lithologic intervals with the greatest promise of hosting these elevated critical mineral resources.

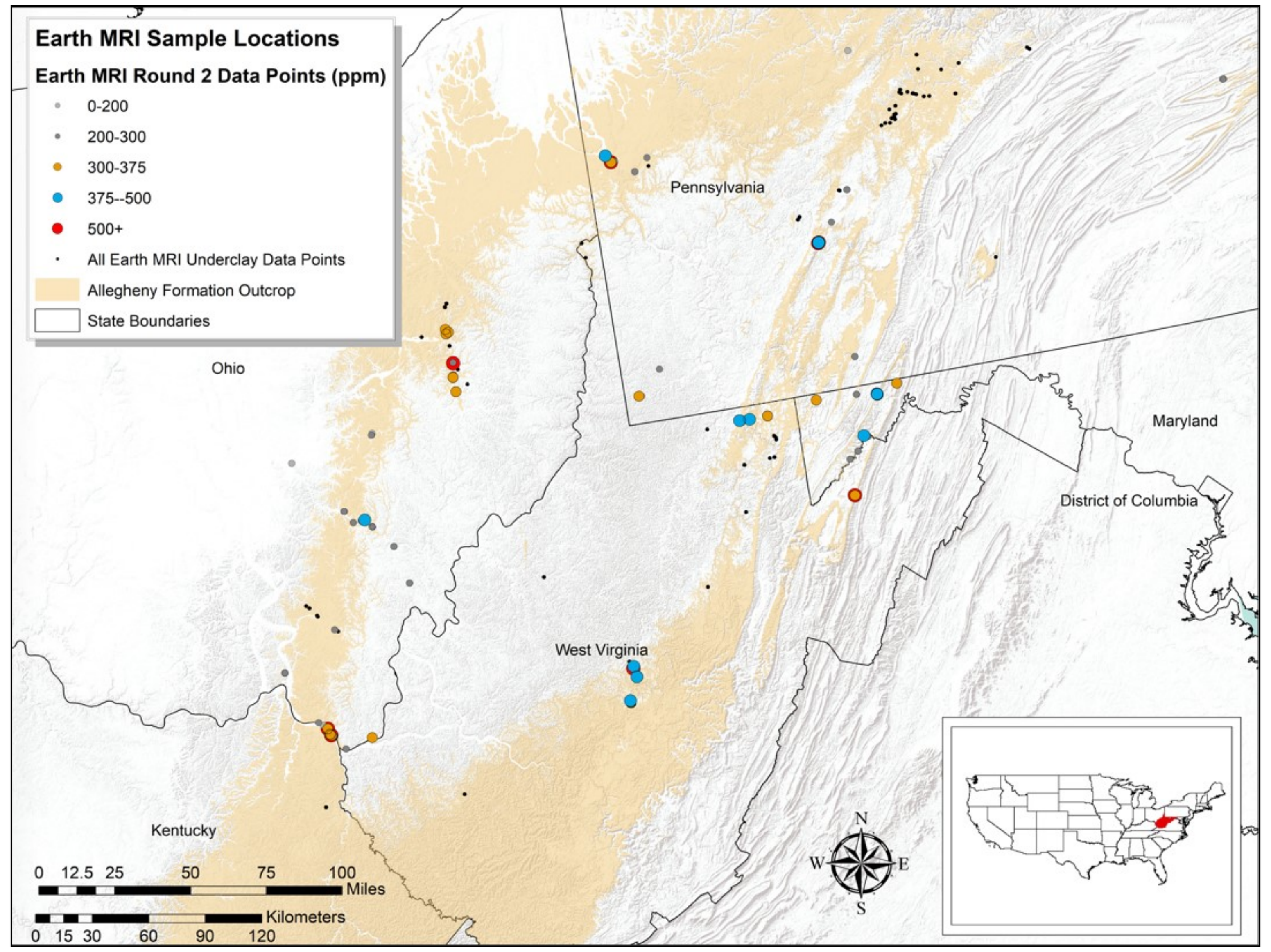
As part of a multi-year study, a stratigraphic and spatially representative set of underclay samples were collected from eight states in the Appalachian and Illinois basins, geochemically analyzed by the USGS, and then processed with Orange, an open-source machine learning and statistical analysis software. Using Orange, Principal Component Analysis (PCA) and cross-plots were created to determine the elements that correlate with higher REE values. The trends indicate that in these samples higher REE totals (>375 ppm) have strong positive correlations with several elements, including Al, P, Th, and Sr, and weakly positive correlations to several others. Higher total REEs were inversely correlated with Mg.

These initial results were then compared with handheld X-Ray Fluorescence (hhXRF) measurements and used to inform the sampling strategy for a second round of sample collection. As a final step, results from each round of sampling will be compared to determine if the screening exercise resulted in higher overall REE totals using the major elemental associations. If successful, this workflow can enable quick-look or field-level selection of samples using the hhXRF and development of a semi-quantitative predictive tool to help locate potential REE deposits.

Predictions tested

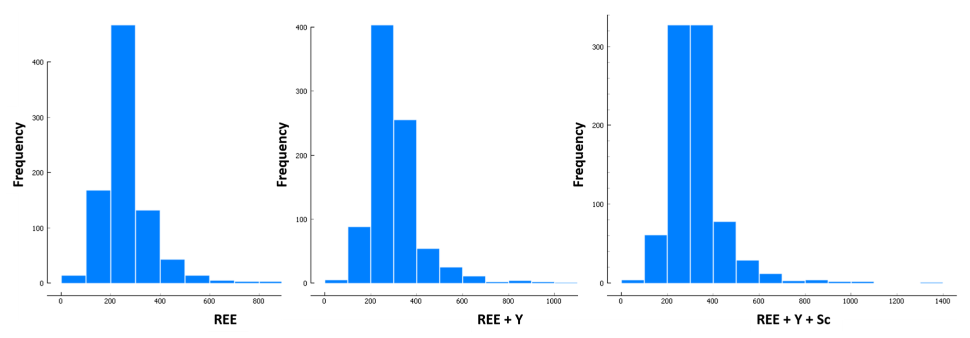
After running Orange through several iterations, some important trends that indicate higher REE totals (> 375 ppm) were found, including:

Weakly positive correlation with total REEs	Strong positive correlation with total REEs	Inverse correlation with total REEs
Bi > 0.7 ppm	Al > 137,500 ppm	Mg < 3800 ppm
Ga > 37.5 ppm	Ba > 670 ppm	
Nb > 20 ppm	Cr > 130 ppm	
Sb > 1.3 ppm	Cu > 56 ppm	
Ti > 7,000 ppm	26,500 ppm > K > 18,750 ppm	
U > 6.5 ppm	P > 500 ppm	
V > 170 ppm	Pb > 39.5 ppm	
	Sr > 500 ppm	
	Th > 20 ppm	



Above: Map of all Earth MRI samples in the Appalachian Basin with the Allegheny Formation outcrop highlighted in gold. Round 2 samples are highlighted by varying concentrations of REEs. To accommodate this study concentration points are broken down to highlight the >300 ppm and >375 ppm values.

	Maryland	Ohio	Pennsylvania	West Virginia
Total Samples Tested	120	128	47	74
Samples with > 300 ppm REEs USGS	16	27	9	25



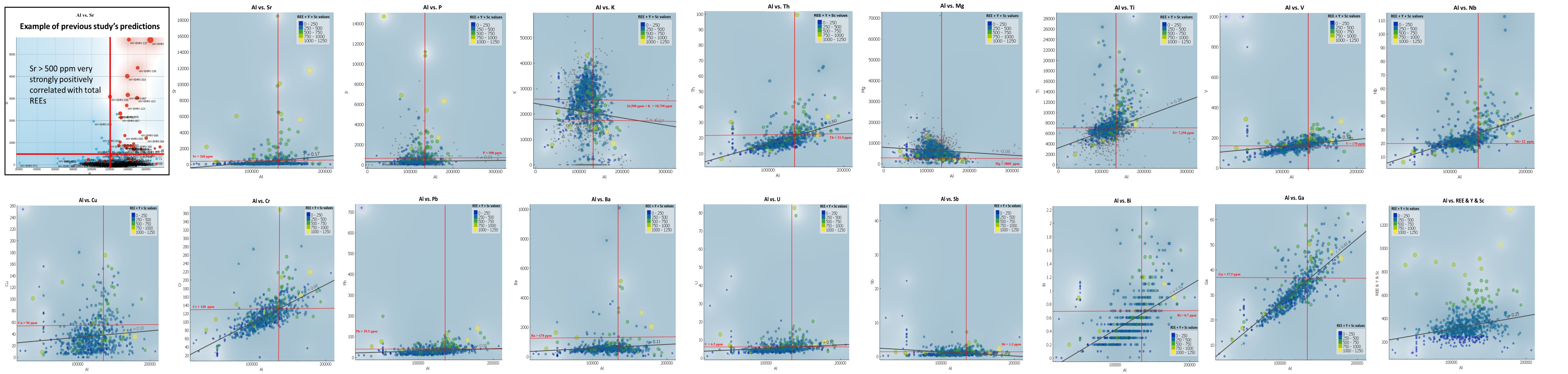
Above: Table of EMRI Round 2 samples per state and number of samples with high REE over 300 ppm with distribution charts of EMRI Round 2 samples broken down by total REEs, REEs + Y, and REEs+ Y +Sc.

Right: Paleogeographic reconstruction map of North America during the Middle Pennsylvanian, the time period for the samples collected. Created by Dr. Ron Blakey. Red star placed over West Virginia for location context.

Explanation of charts below

These cross-plots were made in Orange, mimicking the work flow of EMRI Round 1 data that gave the predictions tested (far left text box). All data plotted below is from the USGS via ACAT Labs with regression lines and r^2 values. The vertical red lines are the predicted value for Al on the x-axis, Al > 137,500 ppm. The horizontal red lines are the predicted value for the element on the y-axis (Predicted value in red beside horizontal line). The background color and size of the bubbles correspond to the total of REEs + Y + Sc, the higher the value the lighter the color with a larger bubble size. Each graph represents the predictions except the Al vs. REEs & Y & Sc graph, which has REE + Y + Sc shading scheme, to show the relationship between Aluminum and the REEs.

Earth MRI Round Two Prediction Cross-plots



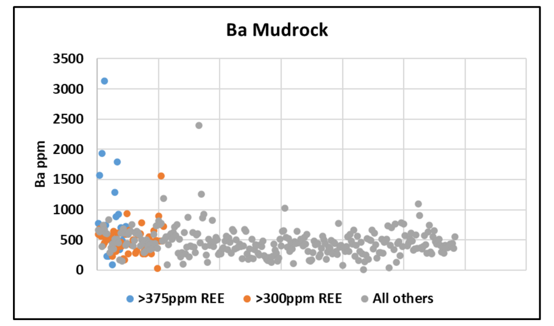
Discussion

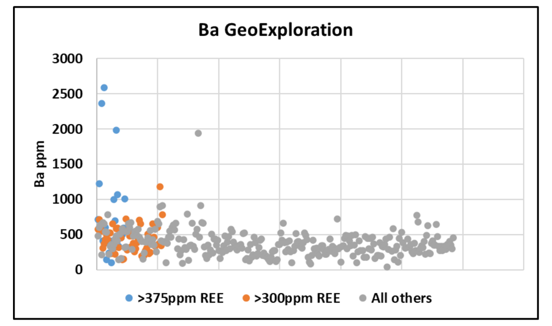
While predictions from the PCA and cross plots utilizing Orange are accurate for some samples, that is not the case for all or the majority high REE samples. Therefore, future work will involve compiling the complete set of the Earth MRI results from this study into the Orange software to determine if further predictions can be constrained. A more concentrated effort to determine the weathering characteristics of the regional underclays and confining the predictions to those elements could also help build better predictions.

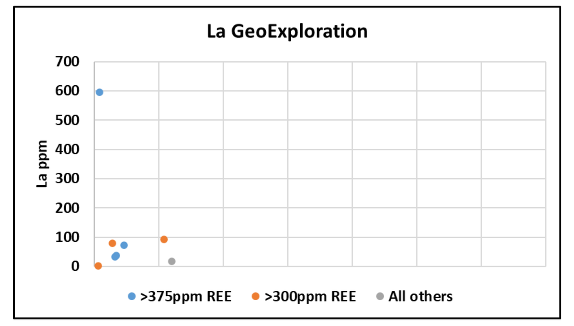
With the ICP-OES-MS data providing total REE data, comparisons to the hhXRF results were evaluated to find any possible correlations between known high REE samples and the hhXRF elemental data. Based on observations of trends within the hhXRF data in the MudrockAir Dual calibration, 6 elements produced high REEs: Ba > 1200 ppm, Ga > 63 ppm, Nb > 50 ppm, Sr > 350 ppm, Th > 50ppm, and Y > 55 ppm. The observations of trends within the hhXRF data in the GeoExploration calibration found 9 elements that produced high REEs: Ba > 1000ppm, Ce > 75 ppm, Ga > 40 ppm, La > 30 ppm, P > 3000 ppm, Sr > 500 ppm, Th > 70 ppm, U > 50 ppm, and V > 600 ppm. Future work will involve analyzing recently returned EMRI round 1 samples with the hhXRF and comparing known high REE samples to those results to see if the observations in this study hold true.

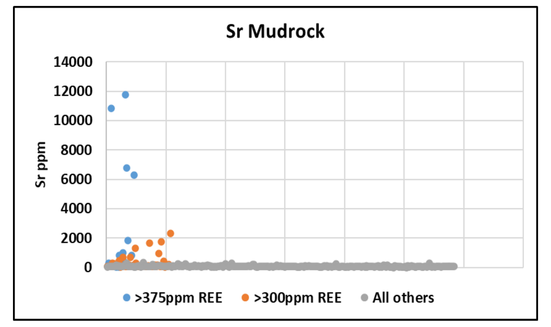
hhXRF Observations

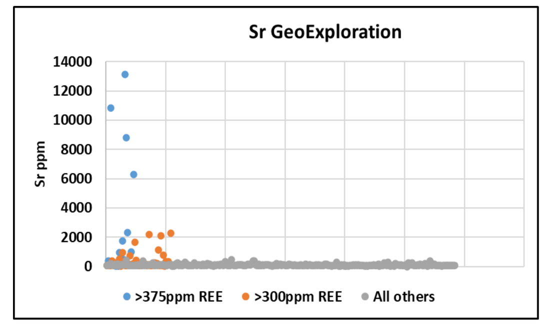
	GeoExploration		MudrockAir Dual
Ba	> 1000 ppm	Ba	> 1200 ppm
Ce	> 75 ppm	Ga	> 63 ppm
Ga	> 40 ppm	Nb	> 50 ppm
La	> 30 ppm	Sr	> 350 ppm
P	> 3000 ppm	Th	> 50 ppm
Sr	> 500 ppm	Y	> 55 ppm
Th	> 70 ppm		
U	> 50 ppm		
V	> 600 ppm		











Methods

Orange

Geochemical data (the first round of EMRI data from WV, PA, and eastern KY, recent analyses from other studies in WV and historical datasets were analyzed using multiple statistical and machine-learning features in Orange (Demsar et al., 2013), including Principle Component Analyses (PCA), cluster, k-means, and t-SNE determinations and plots. Orange was also used to create visualizations such as XY cross plots using data analyses workflows and data mining using a combination of components. All data was converted to ppm for analysis.

hhXRF

Semiquantitative X-ray fluorescence (XRF) spectroscopy was used to determine bulk elemental concentrations. Measurements were taken by the author using a Bruker TRACER 5i pXRF spectrometer equipped with a SDD graphene window detector and Rh X-ray tube. Two applications/calibrations were used for this study; MudrockAir Dual and GeoExploration. MudrockAir Dual measurements were analyzed at 90/180 second phase intervals and GeoExploration measurements were analyzed with 60/60/60 second intervals, both with air under an 8mm spot window. MudrockAir Dual is a calibration for sedimentary rocks with the elemental range of Na-U. GeoExploration looks at oxides of certain elements with the elemental range of MgO to U. All data was converted to ppm (parts per million) to test predictions with errors subtracted.

USGS

Analyses completed by Minerals Analytical Chemistry contract laboratory: AGAT Labs. Samples were analyzed with both Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES-MS) and Wavelength Dispersive X-Ray Fluorescence (WDXRF). The combined WDXRF and 60 element packages were provided along with requisite sample processing, appropriate QC samples, duplicates and data validation. To monitor the quality of data generated by the contract laboratory, Quality Control (QC) and duplicate check samples were submitted with each set of samples. All data was converted to ppm to test predictions.

ICP-OES-MS: Sixty elements are determined in rocks, minerals and soils. Samples are fused at 750°C with sodium peroxide and the fusion cake dissolved in a dilute nitric acid. The resulting solution is analyzed by ICP-OES and ICP-MS.

WDXRF: Major elements are determined in rocks by WDXRF. The sample is fused with lithium metaborate/lithium tetraborate flux and the resultant glass disk is introduced into the WDXRF and irradiated by an x-ray tube. The method also provides a gravimetric Loss on Ignition (LOI).

References

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Demsar J, Curk T, Erjavec A, Gorup C, Hocevar T, Milutinovic M, Mozina M, Polajnar M, Toplak M, Staric A, Stajdohar M, Umek L, Zagar L, Zbontar J, Zitnik M, Zupan B (2013) Orange: Data Mining Toolbox in Python, Journal of Machine Learning Research 14(Aug): 2349−2353.

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