Critical Mineral Enrichment, Mineralogy, and Mobility in Pennsylvanian Coal Measures: An Earth MRI Case Study from West Virginia

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Abstract

The U.S. Geological Survey's (USGS) Earth Mapping Resources Initiative (Earth MRI) works to identify mineralized areas or deposits across the United States that may host critical minerals to be utilized as a domestic resource. Aluminum-rich clays associated with coal horizons in Pennsylvanian-age strata occur throughout the Appalachian Plateau Province, the Central Appalachian Basin, and the Illinois Basin and have the potential to be low-grade, large-volume, critical mineral feedstocks. 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 in clay-rich mine roof and floor samples. 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. Led by the West Virginia Geological and Economic Survey (WVGES) and including the participation of eight state geological surveys, a multi-year, regional reconnaissance study collected over one thousand stratigraphic and spatially representative underclay samples in the Appalachian and Illinois Basins. The samples were collected from both core and outcrops and were analyzed by the USGS. Initial results of the geochemical study showed ranges of total REEs from 1,292 ppm to 53 ppm in the Appalachian Basin and 1,205 ppm to 8 ppm in the Illinois Basin. Sampling in West Virginia targeted clay-rich intervals in the Allegheny Formation; total REEs ranged from 924 ppm to 90 ppm. The aluminum concentrations in the samples ranged from 176,000 ppm to 20,900 ppm and lithium concentrations ranged from 1,000 ppm to 12 ppm. REE enrichment was examined by tau plots, which suggest phosphates and/or Al-rich phases exhibit primary controls on REE enrichment, while XRD confirmed that the clays' mineralogical content did not hold any REE associated minerals. More sampling is needed to determine the future extraction potential of these underclays.

Above: Map of the Appalachian Basin Earth MRI sample locations with the Allegheny Formation outcrop highlighted in light blue. Samples show REE+Y values.

Above: Paleogeographic reconstruction map of North America during the Middle Pennsylvanian, the time period for the samples collected. Red star placed over West Virginia for location context. (Blakey, R., 2017, North America, Deep Time Maps, Maps of Ancient Earth. http://www.deeptimemaps.com/north-america/)

Below: Conceptualized process of REE deposition, mobility, and adsorption in Pennsylvanian coal swamps. Figure created by Cortland Eble, Kentucky Geological Survey

XRD Mineralogy

XRD samples were informed from hhXRF, legacy data, and results from Orange to have XRD analyses performed, including Rietveld and clay specification, to determine the mineral forms/species. These samples were selected in order to confirm that the clay is dominantly kaolinite (as indicated by the Chemical Index of Alteration bulk geochemical values) and to check if there are any REE specific minerals in the clay. Initial whole rock data indicates that the majority of the clays are kaolinite, confirmation from XRD shows that the REEs are not contained within bastnaesite, monazite, or other REE bearing minerals but free throughout clays.

6 samples from West Virginia are shown with 10 minerals present in these samples: kaolinite, mica (iilite), chlorite, quartz, jarosite, svanbergite, pyrite, greigite, anatase, and rutile. All 6 samples reported kaolinite, mica (iilite), rutile, and quartz. Anatase and svanbergite were reported in every sample except one each. Pyrite was reported in 2 samples while chlorite, jarosite, and greigite were reported in just 1 sample each. TREE, Yttrium (Y), Scandium (Sc), and Lithium (Li) values are shown below.

TREE values of XRD Samples

Left: Stratigraphic column of Pennsylvanian coal beds, marine zones, and other units. Modified from Blake, et al. 2002.

Fractional Mass Change Calculation (Tau)

Fractional mass change calculation is based on geochemical mass balance between weathered materials and its presumed parent material. Tau is a comparison of ratios of element concentrations, and it is typically calculated for each mobile element at all measured depth intervals within a profile, which when plotted is referred to as a Tau Plot. $\tau_{j,w}$ represents the percent mass change of a mobile element j, in a weathered sample relative to the mass of the same element in the parent rock. It is calculated as:

$$\tau_{j,w} = \frac{C_{j,w} C_{i,p}}{C_{i,p} C_{j,w}} - 1$$

Where C represents the **concentration** of a **mobile element j**, or an **immobile element, i**, in a **weathered sample, w**, or the **parent composition, p**.

Nb is used as the immobile element in this study due to its documented immobility during weathering. Negative τ values indicate a net loss of the mobile element has occurred, positive values indicate a net gain, and a value of zero indicates no net change. A τ value of -1 means the mobile element is 100% depleted relative to the parent composition, while a τ value of 1 indicates the element is 100% enriched relative to the parent composition. Tau values cannot be less than -1 since a net loss greater than 100% is not possible, however positive (enrichment) values can go as high as geologic processes allow.

Tau values were calculated relative to the least weathered sample and thus percent enrichment and depletion should be viewed as estimates.

Mineralogic Influence on REE Enrichment

To determine what phases may be influencing REE enrichment, τFe, τP, and τtAl were compared to τ values for REEs. τFe values are interpreted to reflect the abundance of iron oxides, both as crystalline minerals and amorphous phases. τAl values are interpreted to reflect the abundance of crystalline and amorphous aluminum-rich phases, such as kaolinite, gibbsite, and allophane, while τP values are interpreted to reflect the abundance of phosphates. These elements were chosen because phosphates are known to incorporate REEs, while REEs are known to adsorb onto aluminum-rich phases like kaolinite and in some cases Fe oxides.

Examples of iron oxide (τFe), phosphate (τP), and Al-rich phases (τAl) controlling REE enrichment are shown to the right (plot C). Note how the tau pattern for Fe, P, or Al follows that of the LREEs, MREEs, and/or HREEs, with areas of significant τFe, τ P, or τAl enrichment corresponding with REEs enrichment, and areas of less τFe, τP, or τAl enrichment or depletion corresponding with REEs depletion. In the six units which were sampled the most in this study, phosphates and/or Al-rich phases seem to be the primary controls on REE enrichment, with Fe locally influencing REE content. Phosphates seem to control REEs in most of the zones of greatest enrichment. Fe oxides and Al-rich phases also appear to influence REE enrichment in some of the zones of greatest enrichment, although their influence is less widespread in study samples than that of phosphates. Tau plots suggest Fe may play an important role in highly REE-enriched paleosols.

Examples of Mineralogic Influence on REE Enrichment

A: Example of underclay tau plot showing phosphates influencing REE retention. Middle Kittanning section of West Virginia core 309-055. τ_j refers to the tau value for the element Phosphorus (P). Solid black line at τREE=0 denotes boundary between enrichment and depletion for all plots above. **B:** Example of underclay tau plot showing Al-rich phases influencing REE retention. Upper Kittanning section of West Virginia core 302-072. τ_j refers to the tau value for the element Aluminum (Al). **C:** ~22 ft below Brush Creek coal base section of West Virginia core 308-007 showing multiple mineralogic influences on REE retention. τ_j refers to the tau value for an element, j, shown in the legend. Mineralogic controls on REE distribution can be complex and vary with depth. Sometimes different enrichment peaks in the same section may be influenced by different mineralogic controls. The tau plot suggests iron oxides (represented by τFe) are the primary control on LREE enrichment around 299 ft and 304 ft depth. In contrast, phosphates (represented by τP) appear to control the MREE enrichment near 305 ft depth, and the slight MREE enrichment around 301 ft.

Above: Plots show REE variability with depth for several sampled intervals. (Tau plots, τREE)

Core 308-007

REE mobility can produce complicated variability in REE enrichment and depletion. REE mobility can be seen in coal core 308-007 to the right. Throughout the core are intervals of depletion and enrichment that are controlled by LREEs and MREEs. Three intervals allowed show the top section of the core in more detail. Core 308-007 has 32 sample points which allowed for detailed profile. TREE+Y+Sc values ranged from 487 ppm to 240 ppm and Li values ranging from 304 ppm to 33 ppm.

Light REEs (LREEs; La to Nd)   **Middle REEs (MREEs; Sm to Dy)**   **Heavy REEs (HREEs; Ho to Lu)**

REE Chondrite Plot West Virginia

Above: The USGS provided Chondrite-normalized REE values for each sample based on bulk rock composition. An element's chondrite normalized composition is the ratio of its concentration in the sample to the average CI carbonaceous chondrite. Plots using Boynton (1984) for normalization were created to show variability within their samples. Chondrite curves from West Virginia have a strong trend with some noticeable outliers. The chart also shows that West Virginia has more of an enrichment of light REEs compared to heavy REEs.

Core 309-055

Right: Tau Plot for the coal core 309-055 had an enrichment of up to 159%, ~10' below the Middle Kittanning coal. REE enrichment is seen near the base and middle of the unit while depletion is present at shallower depths. This occurs when REEs bond to colloids and other particles and are transported (translocated) downward by fluids.

Explanation of the enrichment peak from 1460-1480 feet illustrates the different elemental shifts. A stratigraphic log with a core at the top shows repeating layers of mudstones, flintclays, and shales. Tau plot for this interval shows the peak where sample WV-EMRI-204 is located within the core. Sample WV-EMRI-204 had the second highest REE value for West Virginia. XRD results show the precents are not found in REE bearing minerals but free throughout the clays.

WV-EMRI-204

TREE= 923.54

Discussion

Intervals of REE enrichment are present in many of the cores and profiles sampled during this study. The cores with the zones of greatest enrichment relative to the "parent" composition are as follows: 302-072 (up to 168%, unnamed coal; up to 150%, Upper Freeport), 230-092D (up to 131%, Little No. 5 Block Coal), 306-061 (up to 186%, Middle Kittanning), 282-026 (up to 106%, ~35' below Brush Creek Coal), and 309-055 (up to 159%, ~10' below Middle Kittanning).

While LREE enrichment is the most common, MREE and HREE enrichment are also noted. In the six units which were sampled the most in this study, phosphates and/or Al-rich phases seem to be the primary controls on REE enrichment, with Fe locally influencing REE content. Phosphates seem to control REEs in most of the zones of greatest enrichment. Fe oxides and Al-rich phases exerting less widespread influence and Fe potentially playing an important role in highly REE-enriched paleosols. Processes such as biolifting and downward translocation cause an uneven vertical distribution of REEs in units, necessitating a profile-based approach with appropriate sampling intervals to adequately characterize REE enrichment and depletion in a given unit.

Further sampling and analysis in a more localized study area would benefit characterizing REE mobility and enrichment to get a more impactful idea about which critical minerals are present, the abundance, lateral continuity, and their mobility throughout the environment.

Methods