Microanalysis of Rare Earth Elements in Coal Prep Fines

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Introduction

Rare earth elements (REE) are necessary for the advancement of technology and energy applications. The Rare Earth Metals Market is expected to surpass **$20 Billion by 2024**; the demand for product containing REE include those related to renewable energy, computer hard drives, catalysts, and superconductors. Efforts to secure a domestic source of REE require the development of efficient and cost-effective methods for REE extraction from naturally occurring materials (e.g., mined from geologic formations), recycled products, and/or waste streams. The United States consumes more than 900 million tons of coal per year.

- ~2 billion cubic yards of coal refuse in Pennsylvania
- 10 million tons annually in Virginia
- 120 million tons of coal refuse from over 600 coal preparation plants in 21 coal-producing states.

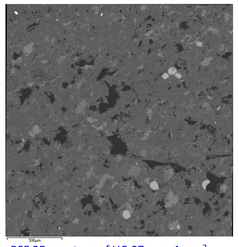
Geologic source of REE amenable to recovery and commercial production → Waste coal

This characterization workflow allowed for the quantification of REE mineral phases in the source rock samples and respective coal fines. This quantitative data and our interpretations will inform future REE extraction techniques and technologies practical for commercial utilization of coal and byproducts generated by mining operations and power plants.

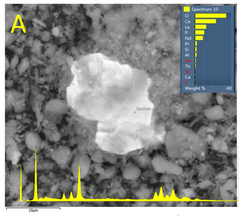
For this study, we focused on samples from the Pittsburgh coal seam and dried ponded fines from the Isabella preparation plant operated by the National Mine Corporation. Multiple microanalytical techniques and image processing techniques were used to investigate the morphology, grain size, presence of mineral phases, and elemental composition of grains/coatings using ***Multimodal microanalytical electron microscopy*** SEM-EDS, EPMA-WDS, FIB-SEM, XRD (bulk unoriented and oriented mounts), and synchrotron based µ-XRF. Quantitative x-ray microanalysis by EDS and WDS was preformed using standard blocks REEP25-15+FC and Geller #489.

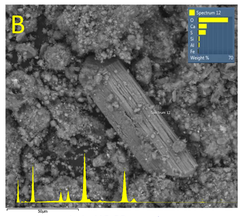
Electron Microscopy & Image Processing

Backscattered electron (BSE) images and elemental x-ray maps were collected on single fields of view and/or were montaged at 400x (0.10-0.12 micrometer/pixel). PerGeos® was used for image processing and segmentation of phases to determine the distribution and occurrence. The Pittsburgh formation is a low porosity material (2-6% by volume) with a distribution of REY mineral phases equal to 1.5-2.4 % volume. REY-bearing mineral phases are associated with clay and ion-exchangeable are not detectable via SEM-EDS; EPMA can detect in certain concentrations although other methods are required.

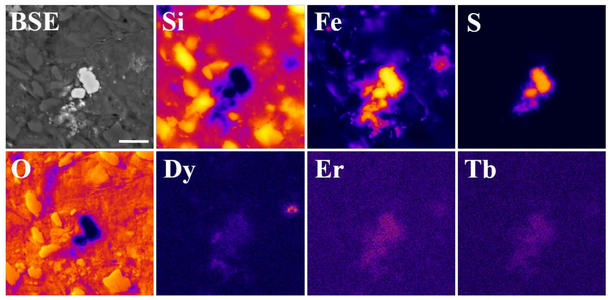


BSE 2D montage of UC-07 over 4 mm²

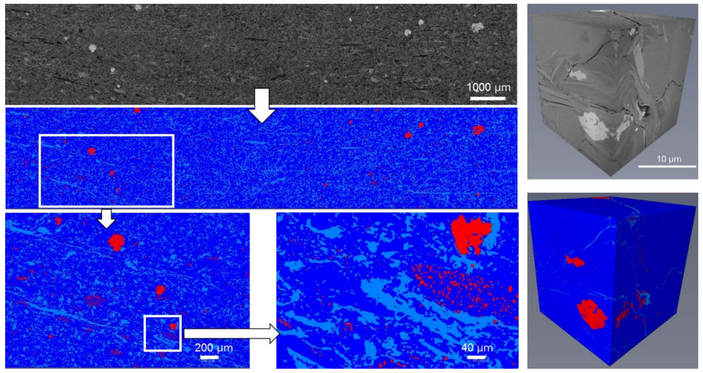




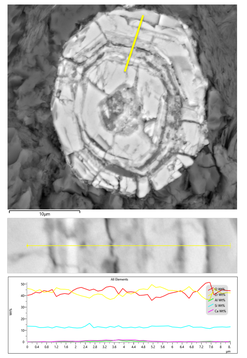
A – BSE image and EDS spectra of REE-bearing monazite grain in UC-09 sample
B – BSE image and EDS spectra of $CaSO_4$ (anhydrite) mineral grain in UC-09 sample

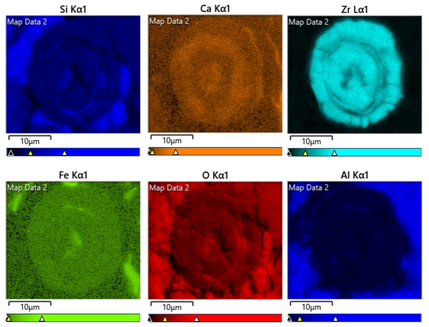


EPMA-WDS quantitative elemental mapping of Pittsburgh underclay (UC-07). Scale bar is 10 microns. Analysis conditions 20 keV, 45 nA, map dwell time=250ms.



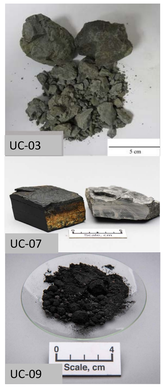
2D montage and 3D segmentation of the Pittsburgh underclay (UC-07). Light blue = pores, dark blue = matrix (quartz and clay), and red = siderite and REY-bearing phases





BSE + EDS maps of a zircon grain in the Pittsburgh underclay (UC-07).
Scale bar is 10 microns.

Characterization Results



Photographs of underclay rock samples analyzed in this study. The sample identification number is shown in the bottom left corner of each panel.

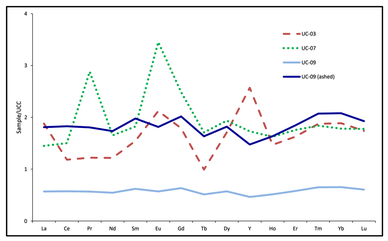
Characterize and quantify REE-bearing minerals in underclay rock from domestic coal producing rock formations.

Identify coal waste due to high enrichment in clay or shale with salable REE concentrations.

- Pittsburgh formation contains clay (Illite/smectite) with abundant quartz, pyrite, (Fe, Ti) oxide, plagioclase, calcite, and zircon. Pyrite and iron oxide coexist in the underclay and contain Dy, Er, and Tb.
- The Isabella fines are organic-rich ; the inorganic fraction is composed of quartz and clay (kaolinite and illite), K-feldspar, and anhydrite.
- **REE+yttrium (REY) = ~300 ppm**
- The Isabella fines have a mean grain size of 27 µm and 0.2 µm specific surface area.

Sample ID	Type/Origin	∑REE+Y Concentration (mg/kg)	Total C (ppm)
UC-03	Underclay/Pittsburgh (West Virginia)	252	3940
UC-07	Underclay/Pittsburgh (W. Pennsylvania)	281	12467
UC-09	Isabella Fines	94/297	17600

Table 1: REE concentrations (mg/kg) in underclay samples reported on whole rock basis from ICP-MS.

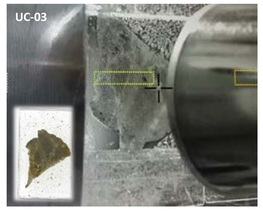


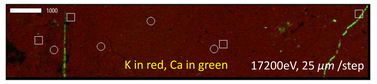
REE (mg/kg) is reported on whole rock basis and normalized to upper continental crust (UCC) values.

	CLAYS				NON-CLAYS					
Sample ID	Halloysite	Kaolinite	Smectite	Illite	Qtz	Kspar	Plag	Calcite	Ilmenite	S species (pyrite, anhydrite)
UC-03			In	Mn	Mn	Tr	Tr	Mn	Mn	Tr
UC-07A coal		Mn	Mn		In			Tr		
UC-07B underclay	Mn	Mn		Mn	Ma	Tr			Tr	Tr
UC-09		In		In	In	Mn				Tr

Table 2: Semi-Quantitative XRD results for underclay samples.
Ma-In-Mn-Tr; Major (>50%)-Intermediate (25-50%)-Minor (5-25%)-Trace (<5%).

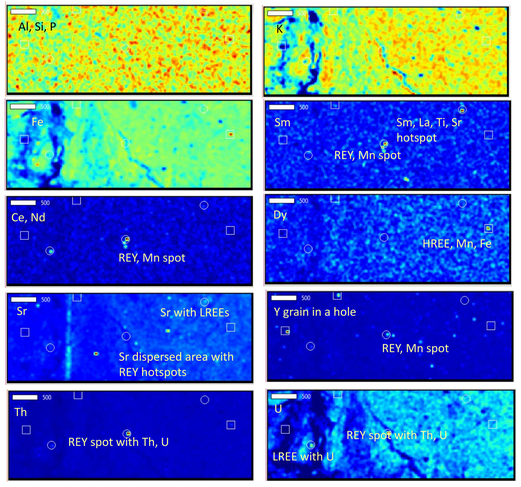
Complementary Synchrotron





Above: µXANES Large scale distribution of fine grain matrix with transecting pyrite and calcite veins. All hotspots are less than 25 µm size (single pixel data)
Y and HREEs (empty squares) have different distribution from LREEs (empty circles).

Left: Thin section and instrument camera view to characterize REE distribution and speciation in clay deposits.



µXRF maps UC-03. Scale bar is 500 µm. No particular co-location between REE and other major elements at 25 µm resolution. Some of the hotspots are likely to be associated with micro/nano phosphates. Select REY hotspots are found to co-localize with Sr, Mn, and Fes.

Summary

Advanced characterization of **underclay** and **fines** provided information on bulk mineralogy, 3D mineral distributions, and estimates of **porosity**.

Pittsburgh underclay and fines contain **REY-bearing minerals**, but these make up a small fraction of the volumes analyzed.

The majority of **REY** are likely in exchangeable form within clay and novel separation technologies will be required. Coal rich fines require additional processing (ashing) to **concentrate** REY for extraction.

Targeting select coal seams & waste products has economic promise.

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