Microanalytical Characterization of Rare Earth Elements in Coal-associated Clays

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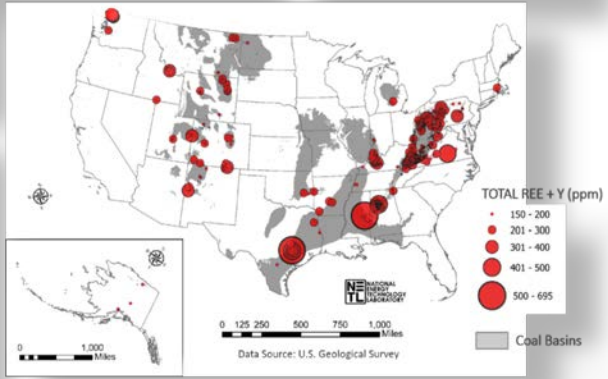
September 5, 2019

2019 International Pittsburgh Coal Conference

Rare Earth Metals Market

The search for a secure and economically viable domestic source



- The Rare Earth Metals Market is expected to surpass **$20 Billion by 2024**;
  - Renewable energy, magnets, computer hard drives, catalysts, and superconductors… etc
- Increasing demand from energy and technological applications.
- Limited domestic supply requires identifying viable resources and development of innovative, cost effective technologies.

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

REEE in Sedimentary Deposits

Sediment hosted REE metals

- Paleogeography of several location in the US have extensively weathered granitic rocks and mobilized REEs as compared to Chinese sources where 60-90% of REEs are ion-adsorbed = 200 tons of REE (Zhi Li & Yang, 2014)

- Vertical variability of clay and mudstone properties

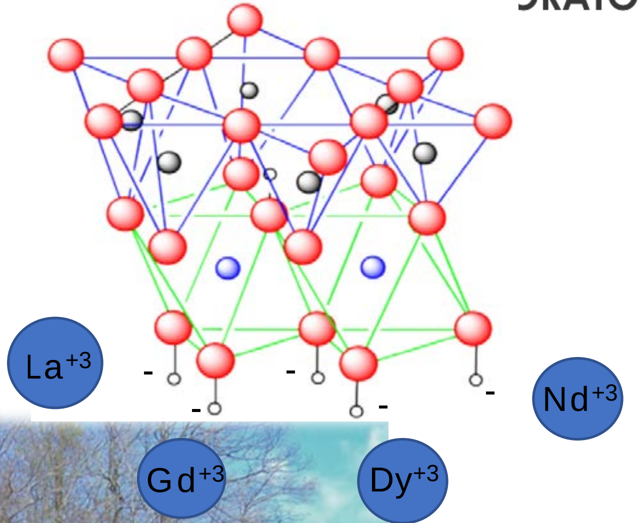
Mobilized from breakdown of primary REE bearing minerals and redeposited as secondary minerals, colloids, or adsorbed on other minerals.

- **Mineral**, part of solid fine particles with same mineral matrix as the host rock
- **Colloid**, insoluble oxy-hydroxides part of polymeric organometallic compounds
- **Exchangeable**, as cations on surface and edge sites of clay or carbonate minerals.

Coal waste & underclay as a feedstock

The search for a secure and economically viable domestic source

- The United States consumes more than 900 million tons of coal per year.
  - ~2 billion yards^3 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 strata related to coal seams – underclay or seat rock – and mine waste rock are viable sources of REE.
- **Ion absorbed REE** from coal producing formations in West Virginia and Western Pennsylvania.



(Schaller, n.d.)

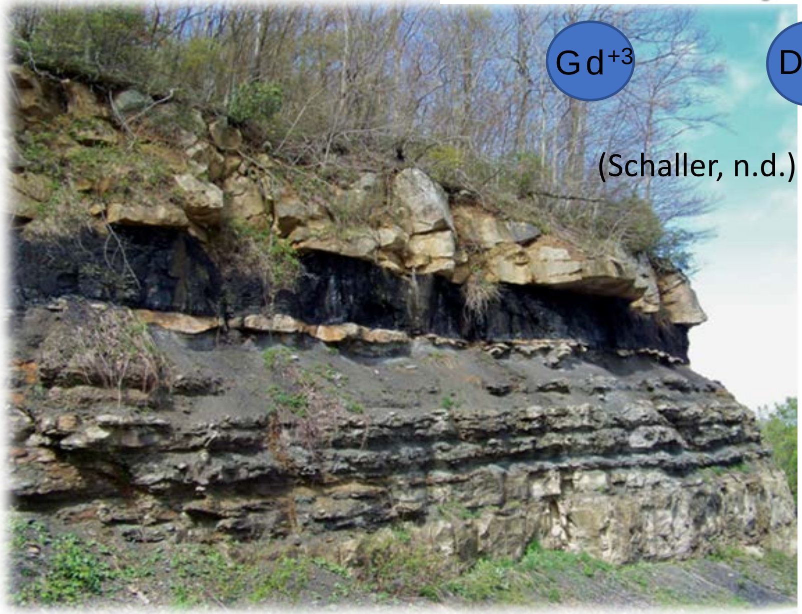


Photo from https://www.flickr.com/photos/piedmont_fossil/5710636433

Up to 50% of coal mined is left on the ground as waste.

Understanding the where and how

Central Appalachian Basin possible feedstocks

- 8 underclay or reject rock (coal fines)

Sample ID	Type/Origin	∑REE+Y Concentration (mg/kg)
UC-01	Underclay, shale/Lower Freeport	296
UC-02	Flint-clay, underclay/Middle Kittanning	457
UC-03	Underclay/Pittsburgh (WV)	252
UC-04	Underclay/5 Block Coal	250
UC-05	Underclay/5 Block Coal	312
UC-06	Paleosol-seat earth/Lower Freeport	333
UC-07	Underclay/Pittsburgh (W. PA)	281
UC-08	Underclay/Brookville	428

Characterize and quantify REE-bearing minerals in underclay rock.

Identify optimal feedstock with salable REE concentrations.

REE concentrations (mg/kg) in underclay samples reported on whole rock basis from ICP-MS (DOE NETL Report: Montross et al., 2018).

Multimodal characterization workflow

Quantification to inform future REE extraction techniques

Underclay Characterization → XRD → SEM → FIB-SEM → EPMA → Synchrotron

FEI Inspect F SEM-EDS + montage operated by Oxford AZtec software

- Post image processing: PerGeos Digital Rock Analysis Software
  - 2D data sets – areal distribution of phases/pore space

JEOL 8530F Plus Hyper Probe EPMA-WDS

- High resolution maps
- Trace element identification

FEI Helios Dual Beam FIB – 600i

- Slice thickness15 nm
  20x20x20 µm
- Post image processing: PerGeos Digital Rock Analysis Software
  - 3D data sets - volumetric estimates of phases/pore space

Synchrotron Stanford Synchrotron Radiation Lightsource (SSRL)

- Bulk X-ray fluorescence (µ-XRF) elemental mapping
  - Deconvolution PyMCA fitting → Sam's Microanalysis Toolkit (SMAK)
- X-ray absorption near edge structure (µ-XANES)
  - Ce reference materials (e.g. Ce(III) chloride, Ce(IV))
  - SIXPACK → ATHENA

SEM/EPMA: standard blocks REEP25-15+FC and Geller #489

Synchrotron methodology in Stuckman et al., 2018 (Int. J. of Coal Geology).

Bulk mineralogy

XRD

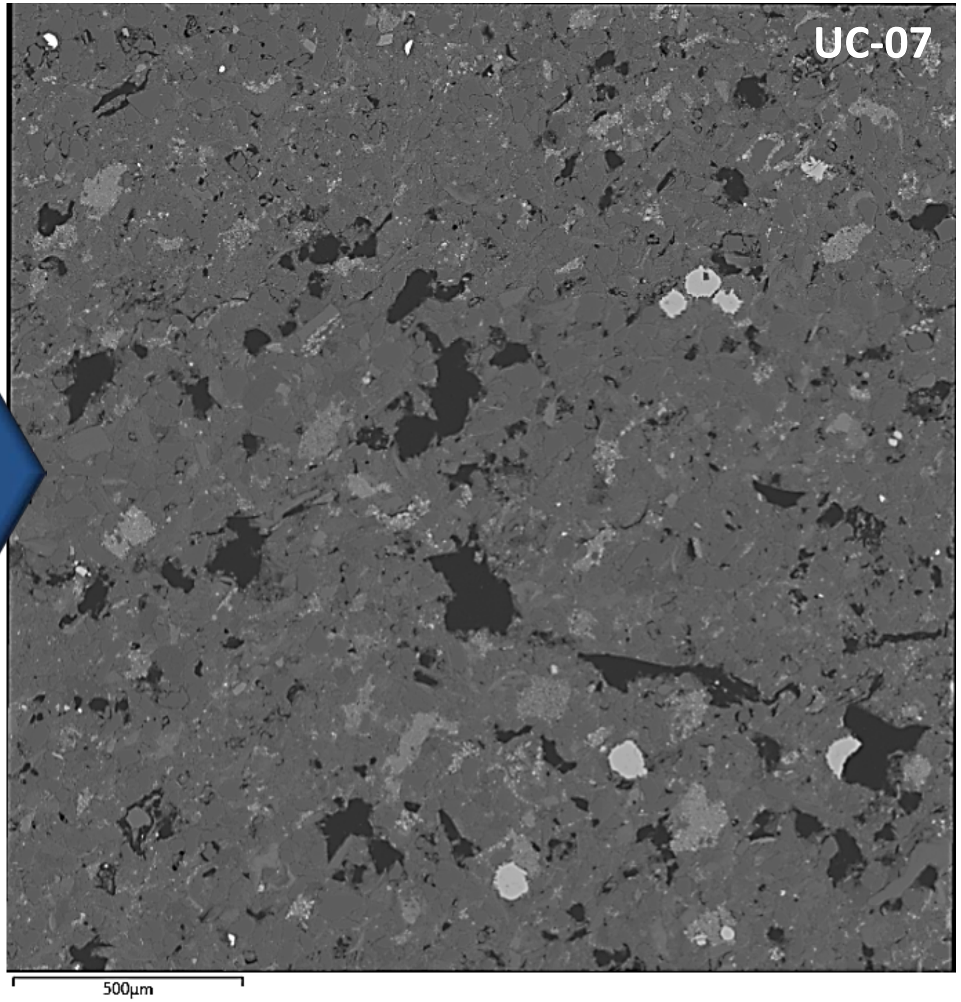
- Powdered and randomly oriented underclay samples
- Main phases: Quartz, calcite, smectite, illite, and halloysite.
- Clays make up more than 55% of the material.

	CLAYS				NON-CLAYS				
Sample ID	Halloysite	Kaolinite	Smectite	Illite	Qtz	Kspar	Plag	Calcite	Ilmenite
UC-01	Mn		In	Mn	Mn	Tr	Tr	Mn	Mn
UC-02	Mn	Mn	Mn	Mn	Mn	Tr	Tr	In	Tr
UC-03			In	Mn	Mn	Tr	Tr	Mn	Mn
UC-04	Mn	Mn	Mn	Mn	Mn	Tr	Tr	Mn	Tr
UC-05	Mn	Mn	In	Mn	Tr	Tr	Tr	Tr	Tr
UC-06	Mn		Mn	Mn	Mn	Tr	Tr	In	Tr
UC-07A		Mn	Mn		In			Tr	
UC-07B	Mn	Mn		Mn	Ma	Tr			Tr
UC-08	Mn	In		Mn	Ma	Tr	Tr	Tr	Tr

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

Petrophysics: minerals; pores; organics

Sources of REE Enrichment



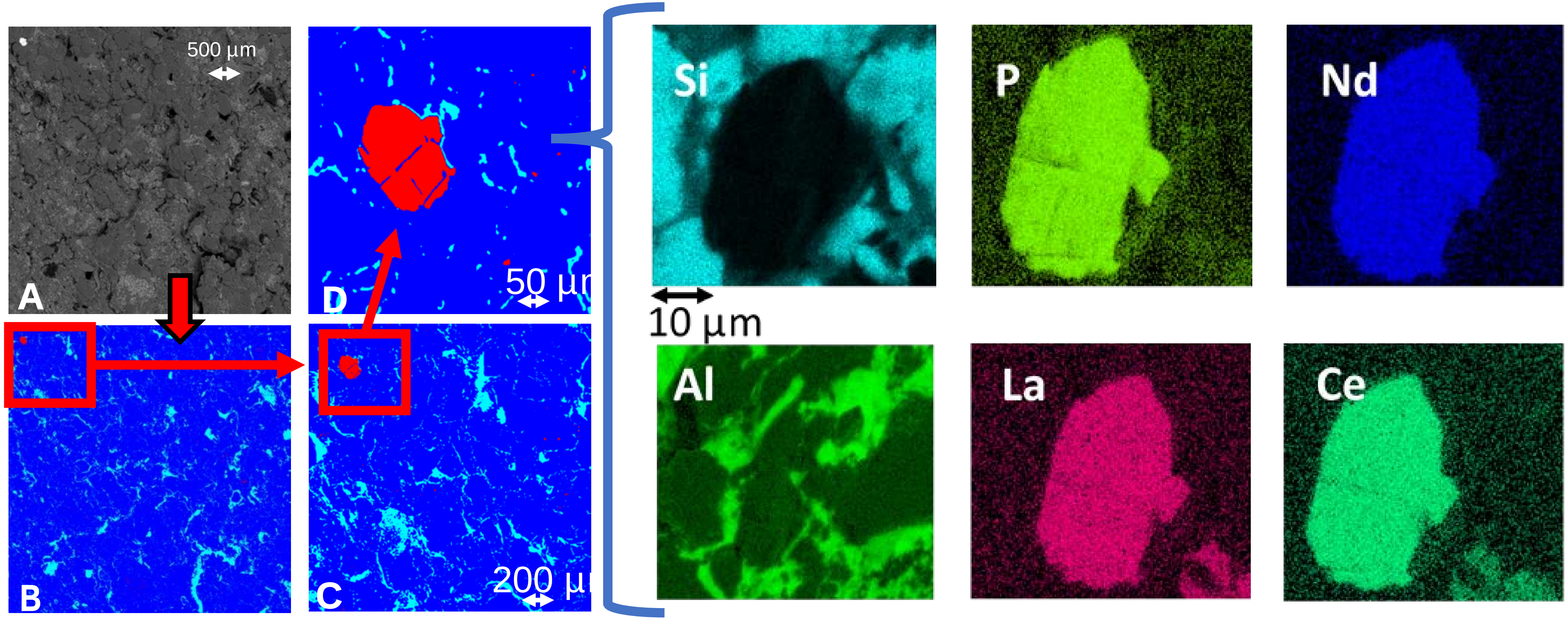
Montage maps coupled with elemental spectroscopy

A workflow to identify petrophysical properties

Isolate the location and distribution on primary REE phases

Advanced Microscopy Workflow

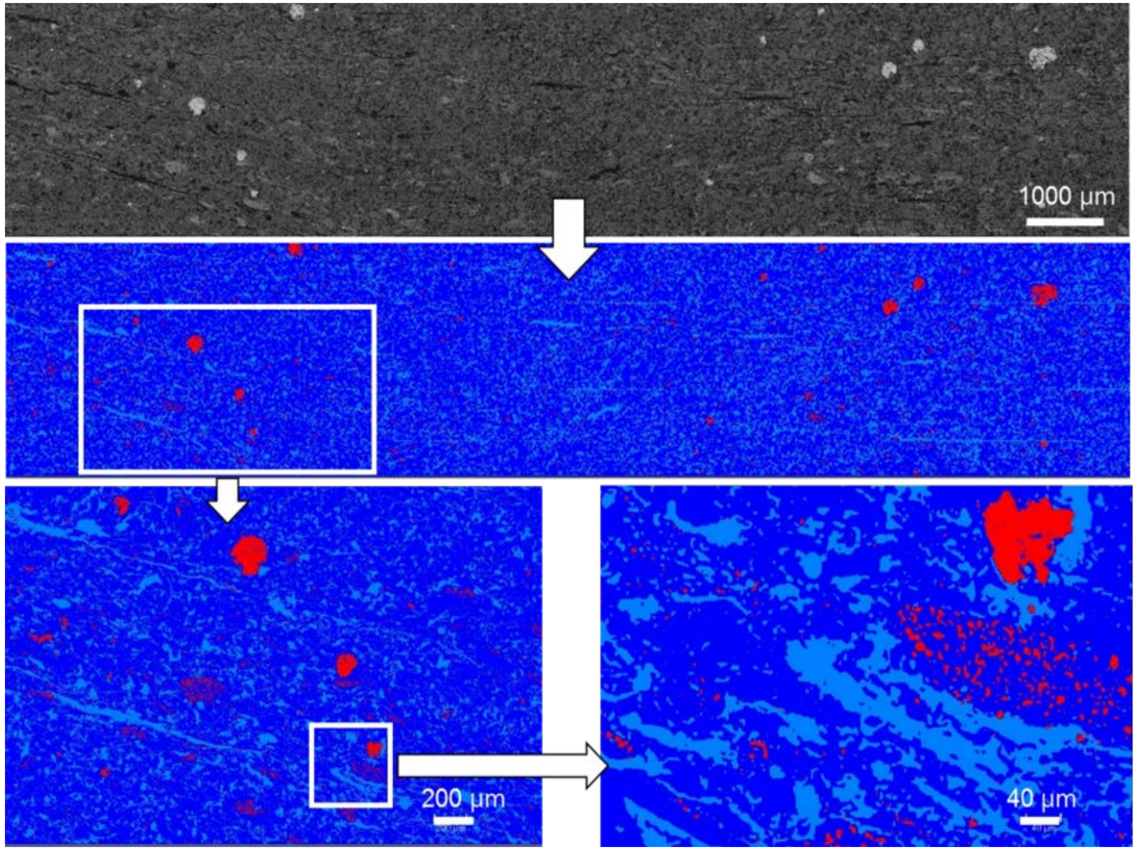
Manual recipe and watershed segmentation



*SEM-EDS map of a rhabdophane ((Ce, La)PO_4*H_2O) grain within the clay matrix of the Pittsburgh coal seatrock (UC-7).*

- By using SEM-EDS we can locate REE phases
- Segmentation of hundreds or thousands of images powered by machine learning and user input

Advanced image processing



Trace mineral
Pyrite (La, Ho, Dy, Lu, Yb, Er)
Chalcopyrite (La, Nd)
Ti-oxide (Lu, Er, Nb)*
Zircon (Lu, Sc)*
Siderite
Galena
Fe-oxide (Er)*
Monazite/ rhabdophane (La, Ce, Nd, Gd)
Xenotime/ churchite (Y, Sm, Eu, Gd, Dy, Er, Tm, Yb)

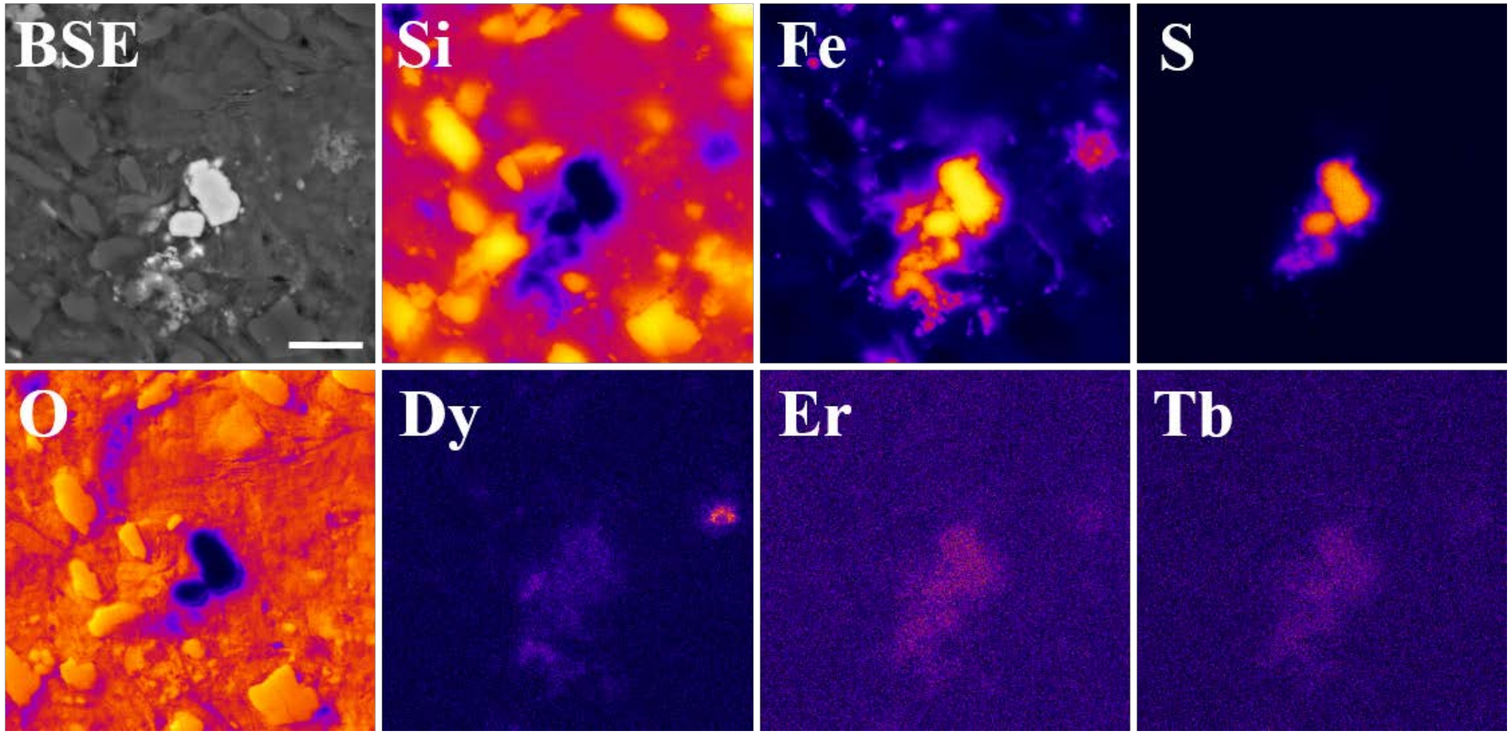
Red = REE-bearing minerals and associated REE

- This method allows for phase identification
- REE phases are most apparent throughout the matrix as <10 µm size grains; particularly as apatite, monazite, rhabdophane.
- Areal distribution shown on slide 13
- Target regions of interest for FIB-SEM

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

A closer look at the chemistry

Microprobe analysis



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.

- Quantify trace elements effectively
- Heavy REEs (Dy, Er, Tb) detected in pyrite grains
- Detect what appears to be nano-minerals within the clay matrix

3D distribution

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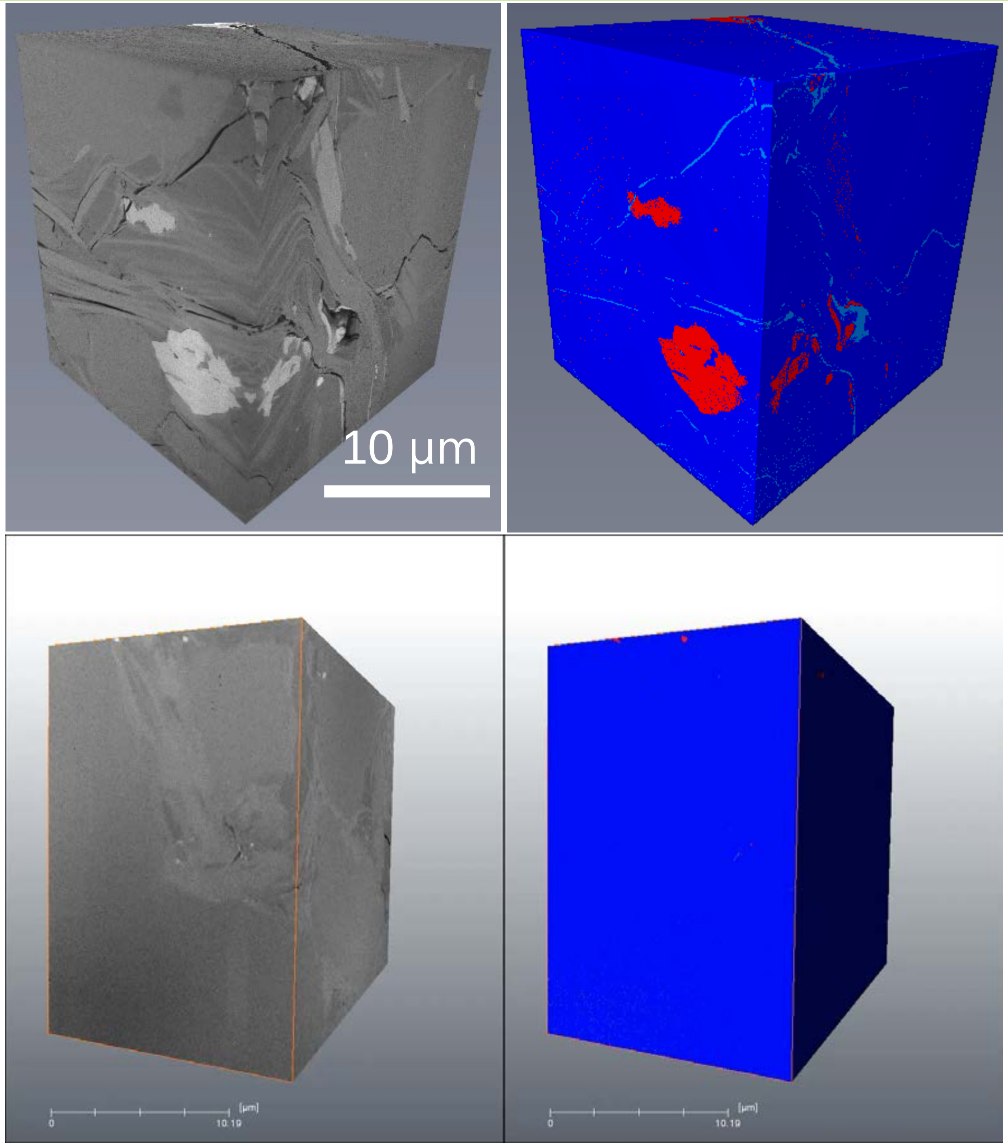
Segmentation

Pittsburgh underclay (UC-07)

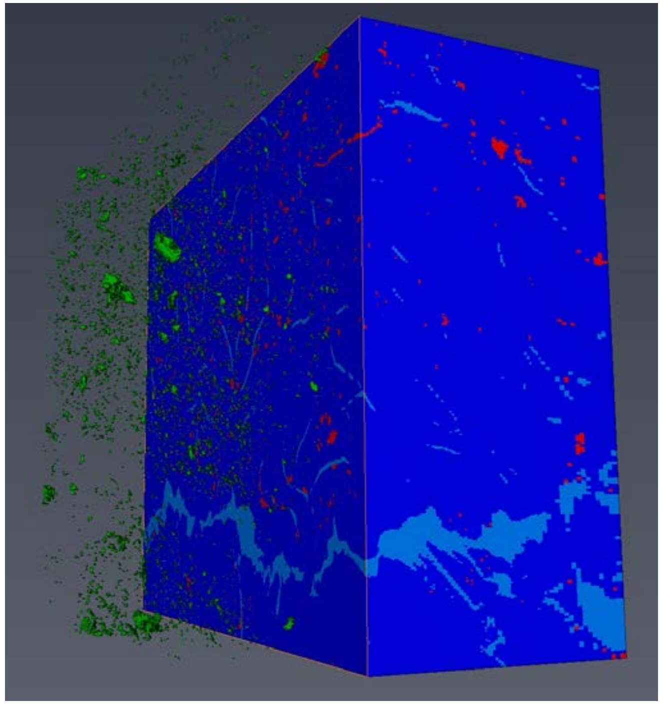
Brookville Underclay (UC-08)



2D & 3D distribution (cont.)

Areal and Volumetric estimations from PerGeos segmentation

- pore space (light blue)
- clay matrix (dark blue)
- high-density minerals (red) *e.g. pyrite, zircon*
- REE-bearing minerals (green) *e.g. monazite*



Sample	Pores + OM	Clay + matrix	High Density Minerals + REE
	Area %		
UC-01	15.0	84.1	0.9
UC-02	2.8	96.4	0.9
UC-03	18.7	80.7	0.2
UC-04	10.4	88.8	1.0
UC-05	2.9	96.9	0.2
UC-06	1.4	81.3	17.1
UC-07	17.4	79.0	3.6
UC-08	11.1	86.0	2.9

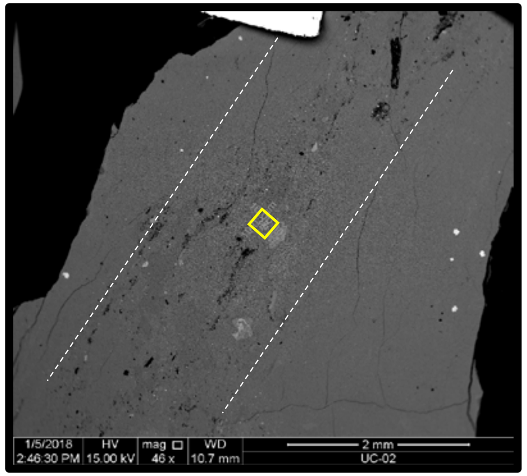
Sample	Pores + OM	Clay + matrix	High Density Minerals + REE
	Volume %		
UC-01	1.3	98.1	0.6
UC-02	20.2	60	20
UC-03	5.7	91.9	2.4
UC-04	N/A		
UC-05	0.2	99.1	0.7
UC-06	0.7	97.2	2.1
UC-07	2.7	95.7	1.5
UC-08	0.3	99.5	0.2

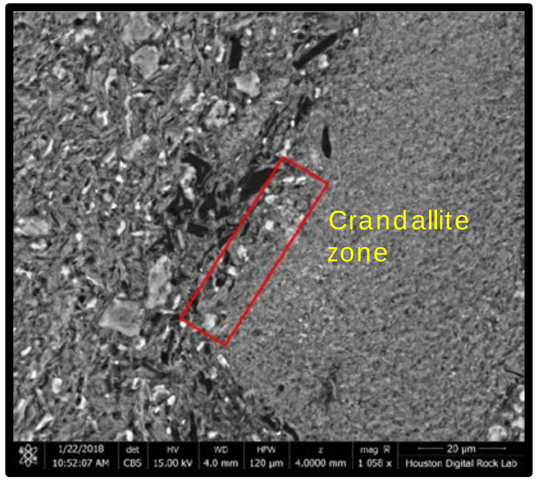
- Average total volume per sample – 9,000 µm^3 (16 total sub-volumes analyzed)
  - Sample heterogeneity, analyses representative of samples, not formation
- Phase segmentation based on grayscale values and informed by morphology and SEM-EDS analyses

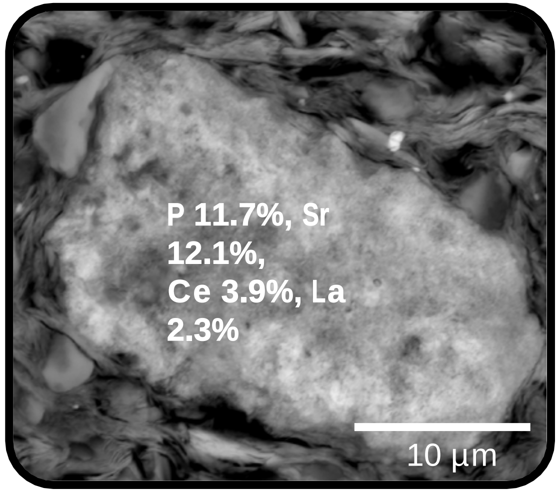
Coal-underclay partings

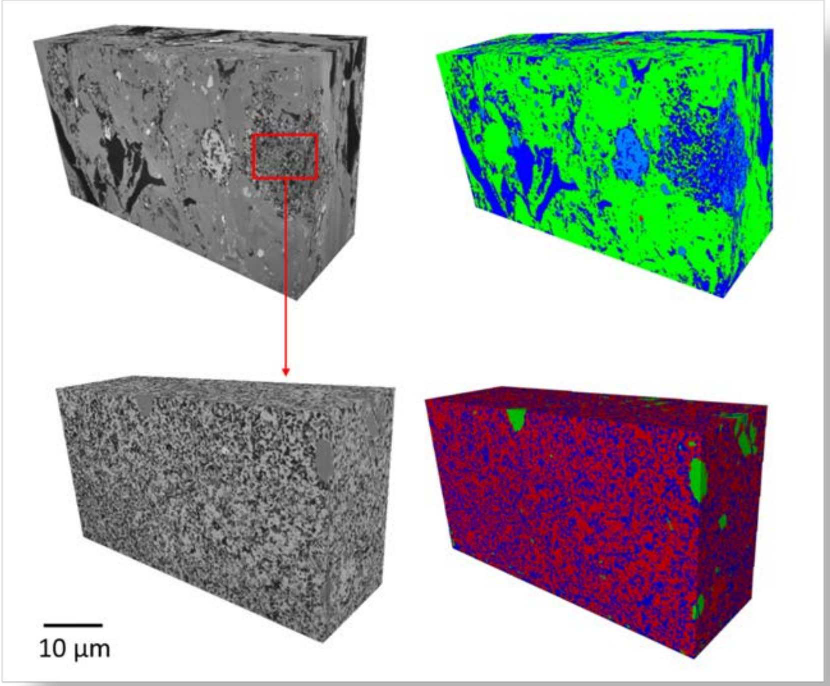
UC-02 Flint Clay Middle Kittanning; Crandallite

- Highest REE = 457 ppm
- Co-located crandallite (illite product) and organics (coal) ranging 5-50 micron sized grains contains LREE, Ba, Sr.
- Ti Oxide/Zircon with Hf (0.5 wt %) and Sc (0.25 to 0.5 wt %)
- Al-PO_4 : REE =Ce, La, Nd
- Cu, Se sulfides contained Pb









Synchrotron micro-analysis (μ-XRF & XANES)

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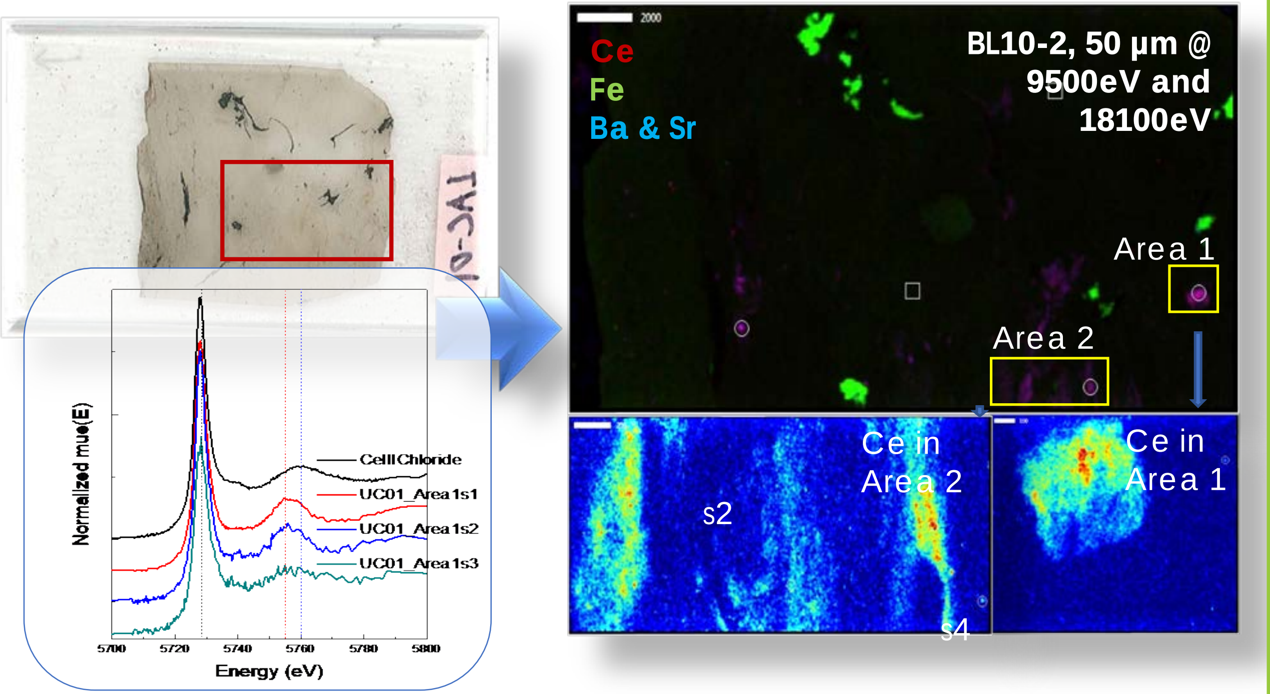
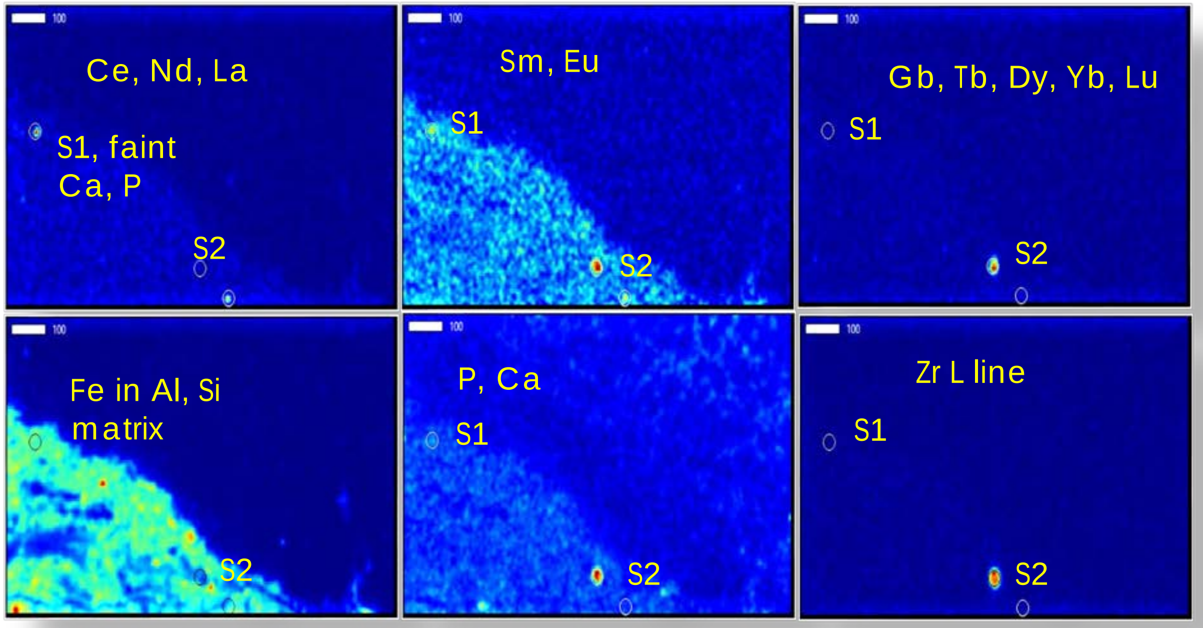
Thin sections UC-01 & UC-04





UC-01

- *μXRF* maps & *μXANES* illustrate large scale Ce distribution in fine grain matrix with visible pyrite and calcite cement.
- Ce co-localized with Sr, Ba
- Bulk Ce L_{III} edge μXANES identified Ce(III) (>85%) as the predominant Ce oxidation state in all samples

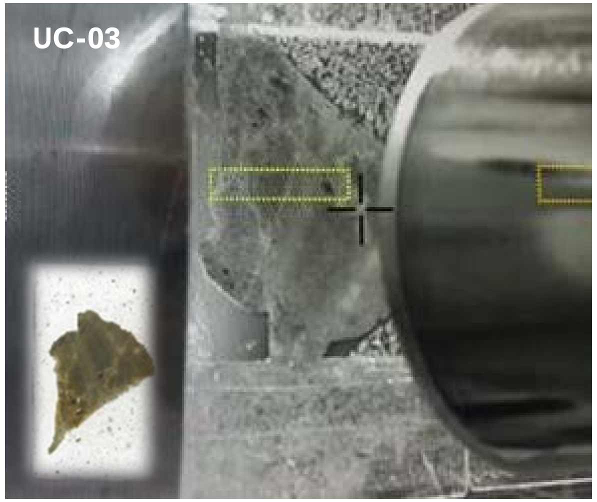
UC-04 *μXANES maps*

- HREE located in zircon grains
- LREE associated with P as well as Ce hotspots (>200 μm) within the clay matrix.

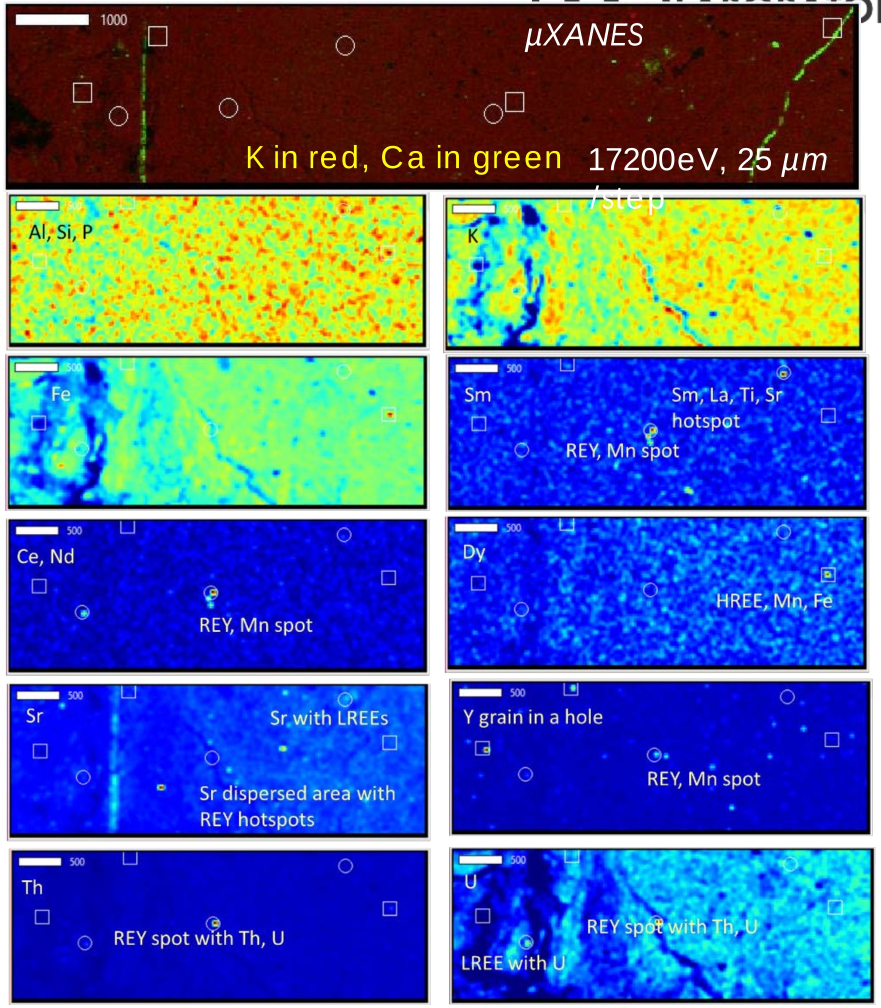
Synchrotron micro-analysis (μ-XRF)

Underclay Thin-section UC-3

- Characterize REE distribution and speciation in the clay deposits.
- REE hotspots tend to be less than 25 *μm* size; Y and HREEs have different distribution from LREEs.
- Majority of REE hotspots do not appear to co-localize with other major elements, but select REY hotspots are found co-colocalize with Sr, Mn and Fe (*μXANES*).
- Some of the hotspots are likely to be associated with micro/nano phosphates.



Above: Large scale distribution of fine grain matrix with transecting pyrite and calcite veins.



μXRF maps of the West Virginia Pittsburgh underclay (UC-03). Scale bar is 500 μm.

Conclusions

Characterization data coupled with advanced image processing were designed to:

1) Determine the bulk mineralogy and clay composition via XRD.
2) Discover REE mineral phases (e.g. monazite (Ce, La, Nd-PO_4) and xenotime (Y-PO_4)).
3) Image the morphology and determine the chemical composition of REE-bearing minerals and other clay bound minerals in the samples.

Our characterization work demonstrates:

- Lower Freeport, Middle Kittanning, 5 Block Coal, Pittsburgh, and Brookville TREE = 250-457 ppm.
- Clay minerals make up >55%: illite, halloysite, and kaolinite
- REE phosphates occur as mineral crystals in the **interparticle pore space** of the underclay or as crystals **embedded** within the matrix clay or massive carbonate mineral deposits.
- REE identified in carbonate and aluminum phosphate **diagenetic minerals**. A portion of the REE are likely in exchangeable form within clay as seen from sequential digest and synchrotron analysis.

Bulk of REE in exchangeable form and will be targeted using novel separation technologies*

*Montross et al presentation session 13: Recovery of REE

Questions?

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https://www.netl.doe.gov/coal/rare-earth-elements

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Acknowledgements

This work was performed in support of the US Department of Energy's Fossil Energy Crosscutting Technology Research Program. The Research was executed through the NETL Research and Innovation Center's Rare Earth Elements portfolio. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

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Paul Zandhuis and Randal Thomas (LRST)

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