Illinois Basin CORE-CM

Critical Minerals Opportunities Within the Illinois Basin

By: Dr. Jared Freiburg, Dr. Charles Bopp, and Mr. Carl Carman

Illinois State Geological Survey

October 25, 2022

U.S. DEPARTMENT OF ENERGY | Office of Science

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Table of Contents

Critical Minerals Opportunities Within the Illinois Basin

By: Jared Freiburg, Charles Bopp,
and Carl Carman
Illinois State Geological Survey
October 25, 2022

This workshop was organized by Jared Freiburg, Charles Bopp, and Carl Carman on belhalf of the Illinois Basin Carbon Ore, Rare Earth, and Critical Mineral Initiative. DE-FOA-0002364

Critical Minerals and Associated Resources in the Illinois Basin: Resource Evaluation, Separation Technologies, and High-value Carbon Products

Moderators: Dr. Jared Freiburg and Dr. Charles Bopp

Mineral resources are the essential raw materials of modern society, powering the production of advanced technologies including the expansion of renewable energy infrastructure. The United States is heavily dependent on mineral imports. Many of these sources are unstable, and their interruption can disrupt important industrial and high technology supply chains. Therefore, the U.S. Geological Survey (USGS) recently designated 50 elements and compounds as “critical minerals” and launched the Earth Mapping Resource Initiative (EMRI) to systematically increase knowledge of the distribution and concentration of these essential resources. The Department of Energy (DOE) began a complimentary effort with the Carbon Ore, Rare Earth and Critical Minerals Initiative (CORE-CM) particularly focused on recovery of critical minerals from byproducts of the extraction and industrial use of coal. This workshop will explore recent efforts from both the CORE-CM and EarthMRI programs to evaluate critical mineral resources in and around the Illinois Basin, demonstrate separation technologies of these resources, and employ associated resources such as carbon to manufacture high-value products.

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Illinois Basin
CORE-CM

Rare Earth Elements and Critical Minerals in coal and coal strata in the Illinois Basin

Franck R.A. Delpomdor
Charles J. IV Bopp

Illinois State Geological Survey, Champaign, IL

Illinois Basin Critical Minerals Short Course
Eastern Section American Association of Petroleum Geologists meeting
Wednesday October 26th 2022

U.S. DEPARTMENT OF ENERGY

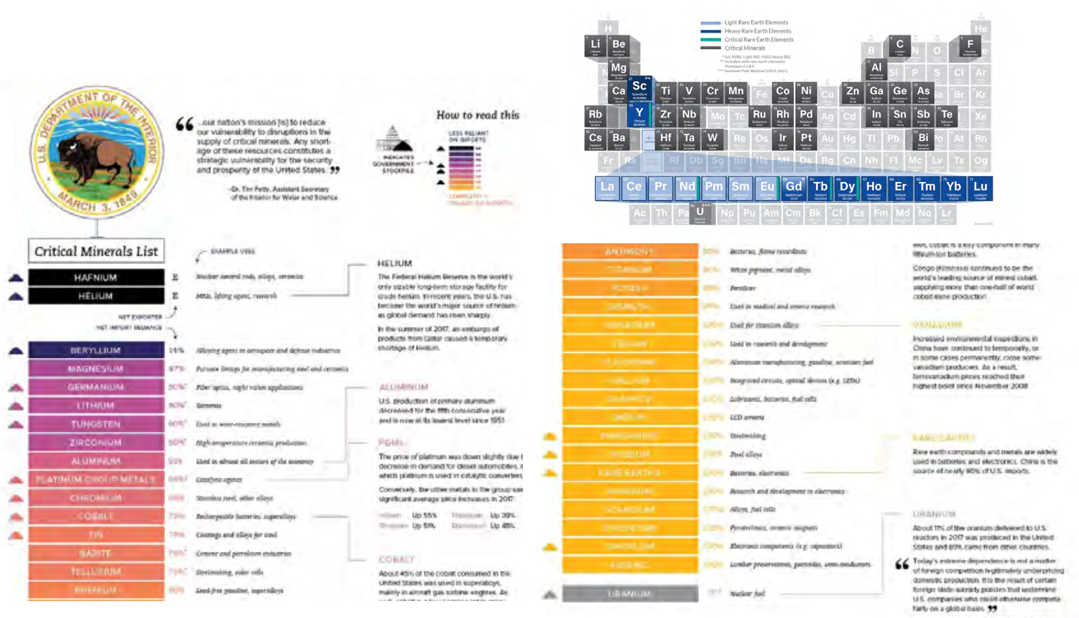
NATIONAL ENERGY TECHNOLOGY LABORATORY

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Introduction

Critical minerals (CMs) were defined by the Energy Act of 2020 as a non-fuel mineral or mineral material essential to the economic or national security of the U.S. and which has a supply chain vulnerable to disruption.

CMs includes copper, lithium, nickel, cobalt and rare earth elements (**REEs**), which are essential components in many of today's rapidly growing clean energy technologies – from wind turbines and electricity networks to electric vehicles.



Source: U.S. Department of Interior. Bureau of Land Management

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

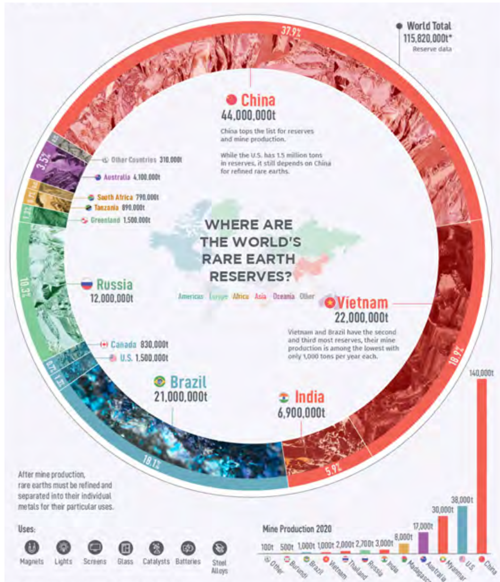
CMs Reserves and Production

37.8% of world **Rare Earth reserves** is located in China (44 Million metric tons), while United States contains 1.3% of REEs

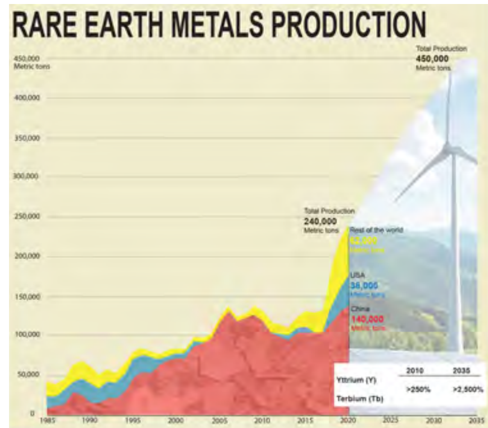
China and other offshore countries produce **over 80%** of the world **Rare Earth metals** production

The demand of Rare Earth metals will increase of 10% for 2035 to over 50% for 2050.

A strategic priority is to resource the production of **REEs** and **CMs** and their associated supply chains back to the U.S. as critical for the U.S. economy and national security



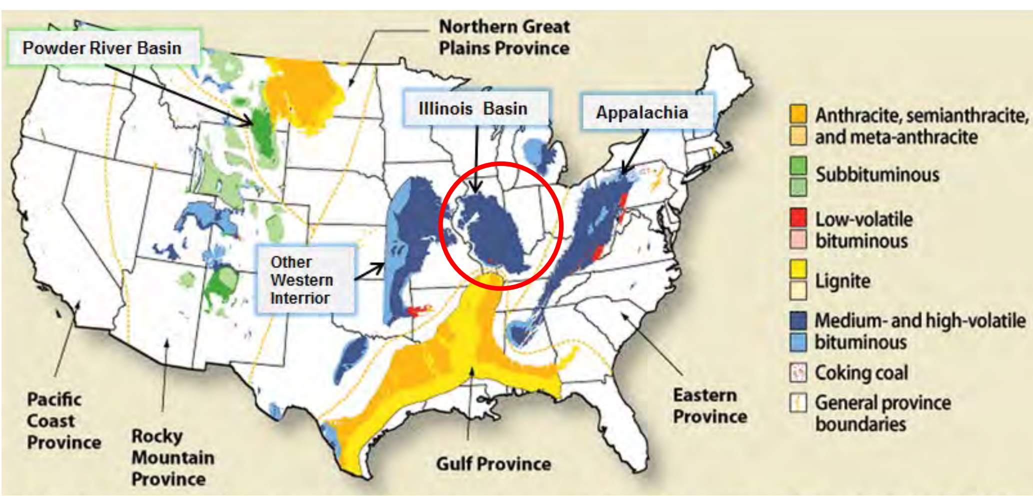
Source: U.S. Geological Survey



Source: IEA, U.S. Geological Survey, Alejo et al. (2012)

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

U.S. Coal Basins



Source: U.S. Energy Information Administration

In 2020, over **485 million metric tons** of coal have been produced in the U.S. aggregate coal mines, in which **13% are produced in the Illinois Basin**

The **demonstrated reserve base in the U.S. Coalfields** is estimated to contain **428 billion metric tons**, in which **23%** is in the **Illinois Basin**

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

REEs and CMs concentrations in the U.S. Coal Basins

Based on the U.S. coal production data from the U.S. Energy Information Administration (2020), an **average REE concentration of 62 ppm in coal**; and assuming 100 percent of the REE in coal can be extracted, separated and recovered; **400 ppm in coal combustion ash**, **62 ppm in coal refuse**, **708 and <0.5 ppm in respectively sludge and raw Acid Mine Drainage (ADM)**

Prototype facilities (feedstock, ADM) could produced annually over 3 metric tons/day of Mixed Rare Earth Oxides based on current production rates

With more than 428 billion metric tons of coal reserves in the United States, **over 15 million metric tons of REEs** are estimated to exist within the remaining coal

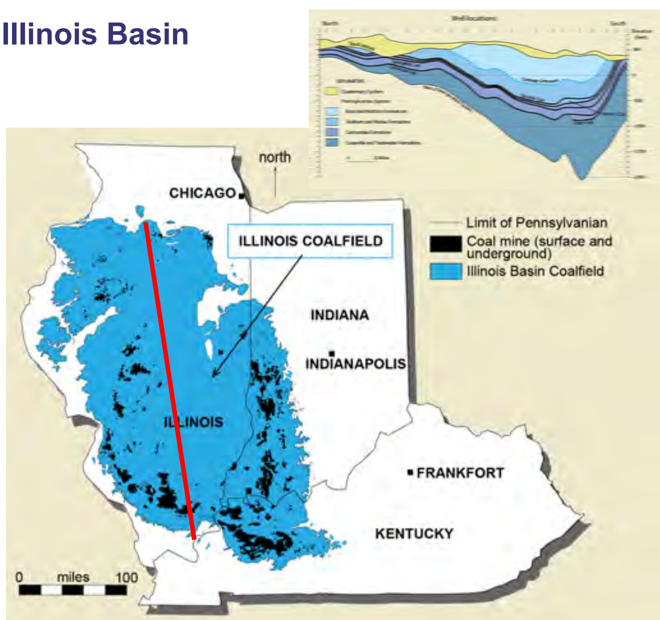
	Coal[1]	Coal Combustion Ash[2]			Coal Refuse[3]		Acid Mine Drainage from Appalachian Basin[4]	
	Domestic Production in 2016 (tons)	Actively Produced (2016)		Landfilled (Since 1991)	Actively Produced (Appalachia)	Landfilled	Sludge	Raw AMD
		Fly ash (tons)	Bottom Ash (tons)	Coal Combustion Products				
Resource Estimate	728,000,000	37,800,000	10,100,000	~1.5 billion tons	~360 million	Estimate: 2 billion tons in PA alone	Unknown	1.5 to 6.6 million gpm
Assumed REE Concentration	at 62 ppm, low side[5]	80 - ~ 1200 ppm (~400 ppm average)[6]			62 - ~700 ppm (low estimate is 62 ppm)		~660 to 750 ppm (708 ppm average)	<0.5 ppm
Potential REE Produced (tons/year)								
100% Recovery	49,800	16,670	4,450	661,000	24,600	136,700	------	807 - 3560
50% Recovery	24,900	8,330	2,230	331,000	12,300	68,300	------	404 - 1780
20% Recovery	10,000	3,330	891	132,000	4,920	27,300	------	161-711
	Most of the Coal is combusted	REE concentrations vary greatly depending upon the coal that is combusted within the power plant. The combustion process increases the REE concentration in the post combustion ash but also makes it more difficult to extract.			REE concentrations vary greatly between layers within a coal seam. This variation can translate to variations within the coal.		Acid mine reclamation sites are distributed throughout a region.	Very low concentrations of REE

1. EIA 2016 Coal Report. https:/www.eia.gov/coal/annual/pdf/acr.pdf
2.The American Coal Ash Association. https:/www.acaa.org/Portals/9Files/PDFs/ACCA-Brochure-Web.pdf
3.Estimated 2/1 ratio of rock and refuse to coal production in Appalachia combined with data from EIA Coal Report
4. Draft report: :Rare earth elements in Appalachian Basin mine drainage". Paul Ziemkiewicz, WVU
5. Finkelman, R. B., 1993. Trace and minor elements in Coal. Org. Geochem. 593-607 (Springer). https:/link.springer.com/chapter/10.1007%2F978-1-4615-2890-6_28
6. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents of black shales and coals. M.P. Ketris, Ya.E. Yudovich

Source: U.S. Geological Survey

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Illinois Basin



Source: Modified from Korose & Elrick (2010)

The coalfields of Illinois, extending in Indiana and west Kentucky constitutes the Eastern Region of the Interior Coal Province, known better as the Illinois Basin (Korose & Elrick 2010).

Based on demonstrated reserve base calculations, approximately **15% of Illinois Basin coal resources are classified as surface minable or strippable**, as defined as mapped coal greater than 18 in. thick and with less than 150 ft of overburden.

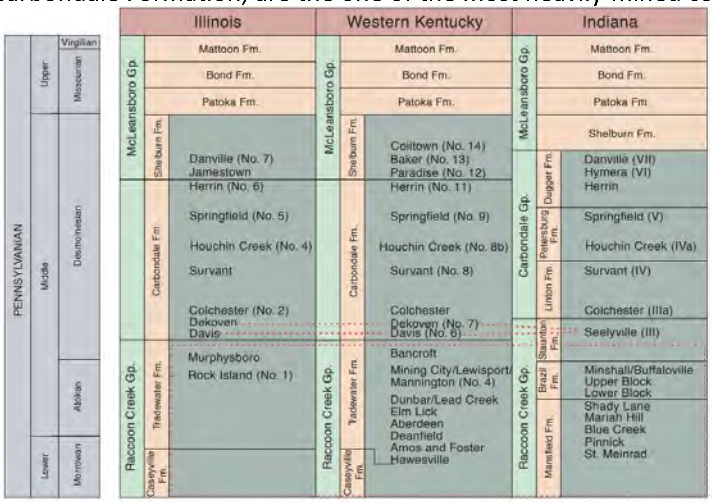
Approximately **85% of Illinois Basin coal resources are classified as underground minable**, which consist of all mapped coal more than 28 in. thick and greater than 150 ft deep.

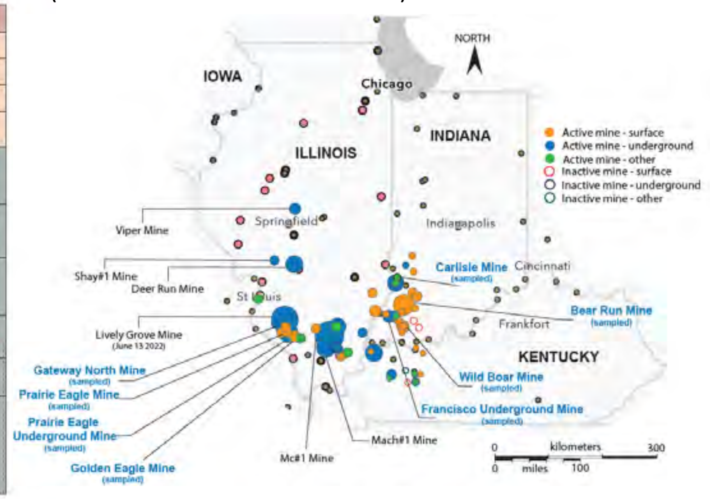
Recoverable coal reserves at producing mines are estimated at **18 and 1,700 million metric tons** for surface and underground minable coals respectively (U.S. Energy Information Administration 2019).

Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Illinois Basin

The Illinois coal resources are concentrated in the Lower and Middle Pennsylvanian strata, in which the upper Carbondale and lower Shelburn Formations contain the majority of resources. Two coal beds, the Herrin and Springfield coals in the upper Carbondale Formation, are the one of the most heavily-mined coals (Reserve: **63 billion metric tons**) in the Illinois Basin.





Source: Hatch & Affolter (2002)

Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

CMs in the Illinois Basin

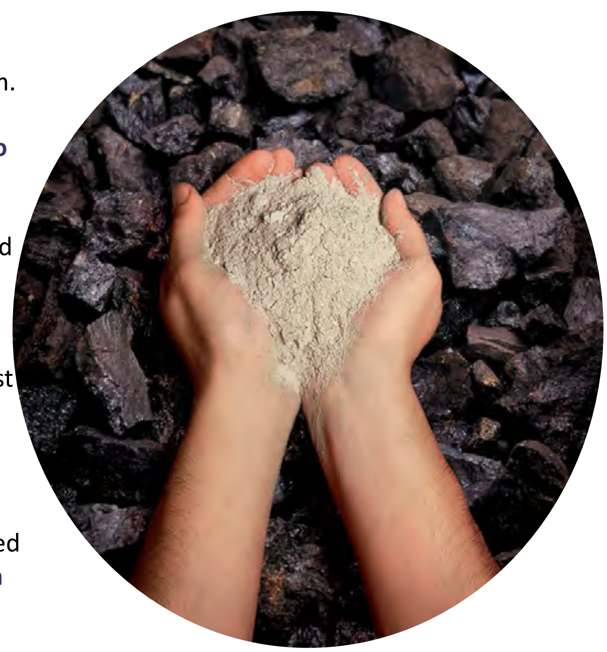
All Illinois coals are significantly enriched in boron, chlorine, and selenium.

REEs commonly occur in amounts up to **0.2% of the whole coal** and **up to 1.5% or more of coal slurry and refuse** (Korose & Elrick 2010).

Lithium leaching recovery from an Illinois basin bituminous coal extracted 70–80% of the lithium using calcination followed by acid leaching with a concentration between **150 and 175 ppm** (Zhang et al. 2020).

Most of the **REE+Y** contents are associated with clay minerals with highest contents around **270 ppm** in the Anna Shale, i.e. the roof rocks of the Herrin coal, and **229 ppm** in the Turner Mine Shale overlying the Springfield coal strata (Valian 2020).

Most black and dark gray Pennsylvanian shales of the U.S. Midwest yielded average **1,300 ppm Zn**, **85 ppm U**, **655 ppm Mo**, **130 ppm Se** and **55 ppm Cd** (Coveney & Glaskock 1989).



ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Illinois Basin (IB) Carbon Ore, Rare Earth and Critical Minerals (CORE-CM) Initiative

Illinois Basin CORE-CM

The **IBCORE-CM** assesses the potential value of natural resources and recovery of **REEs** and other **CMs** from coal and coal by-products

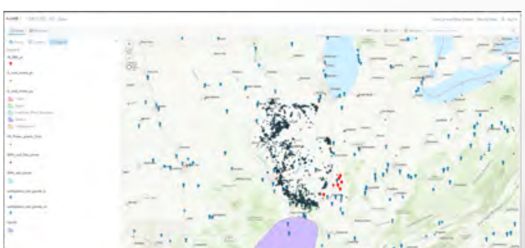
This project is designed to address the upstream and midstream **CMs** supply chain and downstream manufacturing of high-value, nonfuel, carbon-based products

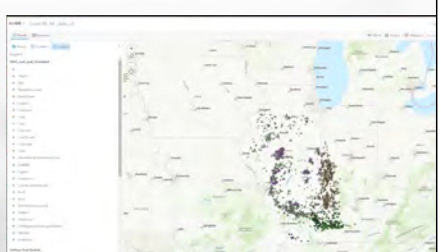
The **IBCORE-CM** catalyze regional economic growth reusing U.S. coals and associated by-products and waste streams from feedstocks for domestic production of **REEs** and **CMs** to enhance our national and economic security

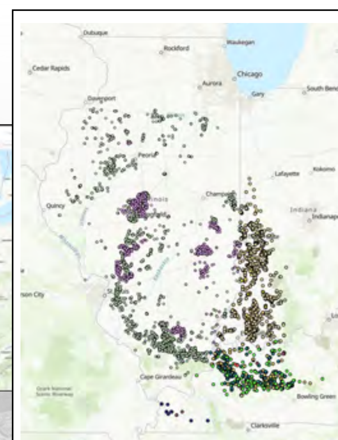
ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Characterization of REEs and CMs Resource Assessments in Coal and Coal Strata Sources

- Develop a comprehensive basinal inventory of **CMs** resources from coal and coal by-product sources to provide industry with a clear understanding of the potential within the Illinois Basin.


active coal mines, coal wastes and by-products


coal quality, critical mineral and REE data

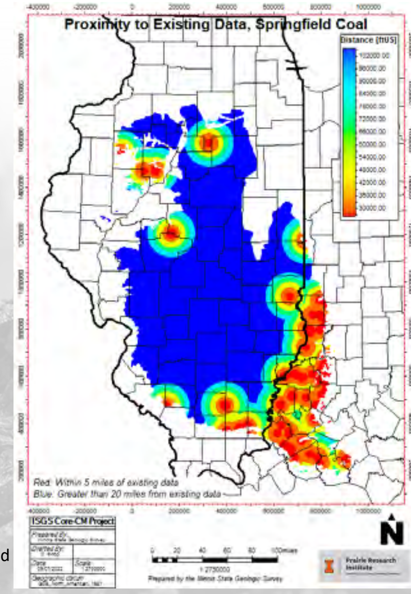


- Understand the opportunity with respect to the primary and co-products of various sources, the resource types, mass/volume estimates, and available existing infrastructure.

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Characterization of REEs and CMs Resource Assessments in Coal and Coal Strata Sources

- Define the gaps in mineral resource information
- Understand the characteristics needed for standard methodologies, and the calculation of uncertainty.
- Conduct analysis on feedstocks and resulting products to reinvigorate manufacturing activities in the basin.



Example of data distribution for the Springfield Coal showing the gaps in the Illinois Coalfield.

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

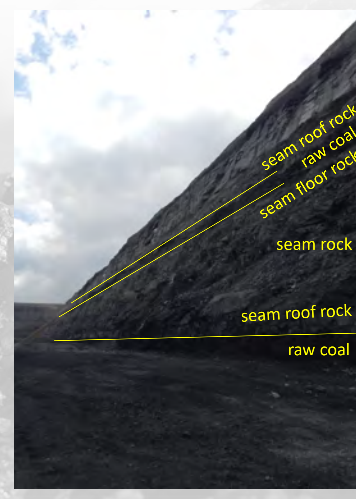
Characterization of REEs and CMs Resource Assessments in Coal and Coal Strata Sources

Additional samples must be collected to provide support for the existence of substantial **CMs** resources existing at concentrations that appear to be technically recoverable in quantities sufficient to supply a robust recovery activity.

Material	Level 1 attribute	Level 2 attribute	Level 3 attribute
coal core	reserves	in-situ	resource evaluation
raw coal	raw coal	extraction	resource production
partings	raw coal	extraction	resource production
seam floor rock	raw coal	extraction	resource production
seam roof rock	raw coal	extraction	resource production
seam rock	raw coal	extraction	resource production
refuse coarse	cleaning	coal preparation	processing
refuse middling	cleaning	coal preparation	processing
refuse fine	cleaning	coal preparation	processing
coal slurry	cleaning	coal preparation	processing
clean coal	cleaning	coal preparation	processing
pulverized coal	combustion processing	feed coal grinding	utilization
pulverized rejects	combustion processing	feed coal grinding	utilization
ash fly	combustion byproducts	energy conversion process	utilization
ash bottom	combustion byproducts	energy conversion process	utilization
ash mixed	combustion byproducts	energy conversion process	utilization
ash landfill	combustion byproducts	waste disposal	waste disposal
ash pond	combustion byproducts	waste disposal	waste disposal
coal mine drainage	waste drainage	waste disposal	waste disposal
coal mine precipitates	waste drainage	waste disposal	waste disposal

Source: NETL

Perry Co, Illinois, API no. I1214528900



ILLINOIS

Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

Characterization of REEs and CMs Resource Assessments in Coal and Coal Strata Sources

Methodology:

All materials from coal preparation, where available, collected raw (as mined), cleaned (prepared), and waste (refuse) coals from the same mine will be collected directly from mined intervals, approximately 50–70 lbs. (20–30 kg) of material from each of 2–4 benches in order to represent an entire coal bed.

Drill cores for the sampling of raw coal, seam floor and roof rocks are recommended if possible.

In preparation plants, 50–70 lbs. (20–30 kg) of material for raw, cleaned, and/or prepared coals will be collected from a stopped belt, if possible, every 20-60 min for a period of 3 h and placing each increment into a common container. If possible, a belt sweep sampler will be used to collect a representative sample of the coarse refuse material.

For the fine refuse material, the sample will be collected periodically in the pump discharge line of the thickener underflow stream. A bulk sample of each waste material will be obtained by taking incremental samples every 20-60 min for a period of 3 h and placing each increment into a common container.

ILLINOIS

Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

Characterization of REEs and CMs Resource Assessments in Coal and Coal Strata Sources

Methodology:

The middlings material will be obtained from the coarse refuse material by subjecting a representative sample of the bulk to a float-sink analysis using a medium having a 1.8 specific gravity. In other cases, representative grab samples of at least approximately 30 lbs. (15 kg) of fresh material will be collected from piles adjacent to operating preparation plants.

Samples obtained will be stored in sealed plastic sample containers and/or sealed plastic storage bags, with as much as a 1 year between sample collection and completion of all analyses. All materials with the highest REE values will be shipped to DOE.

Sample preparation:

All coal and associated coal samples must be crushed, splitted, and powdered according to ASTM D2013 (ASTM 2019a). If Quality Coal data are not given by the Coal company, operator or coal plant, proximate (ASTM D3172; ASTM 2019b) and ultimate (ASTM D3176; ASTM 2019c) coal analysis, and and sulfur forms (ASTM D2492; ASTM 2019d) must be prepared in a laboratory for subsequent bulk geochemical studies.

Analytical method:

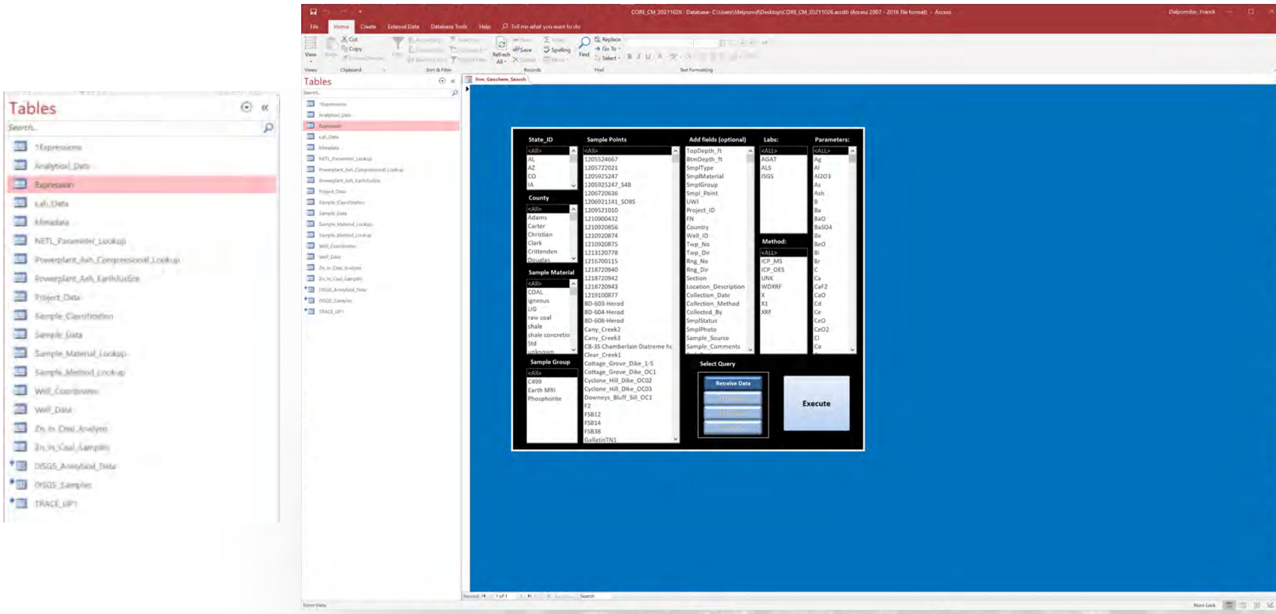
ICP-MS

ILLINOIS

Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

Database Integration, Toolsets, Modeling and Instrumentation

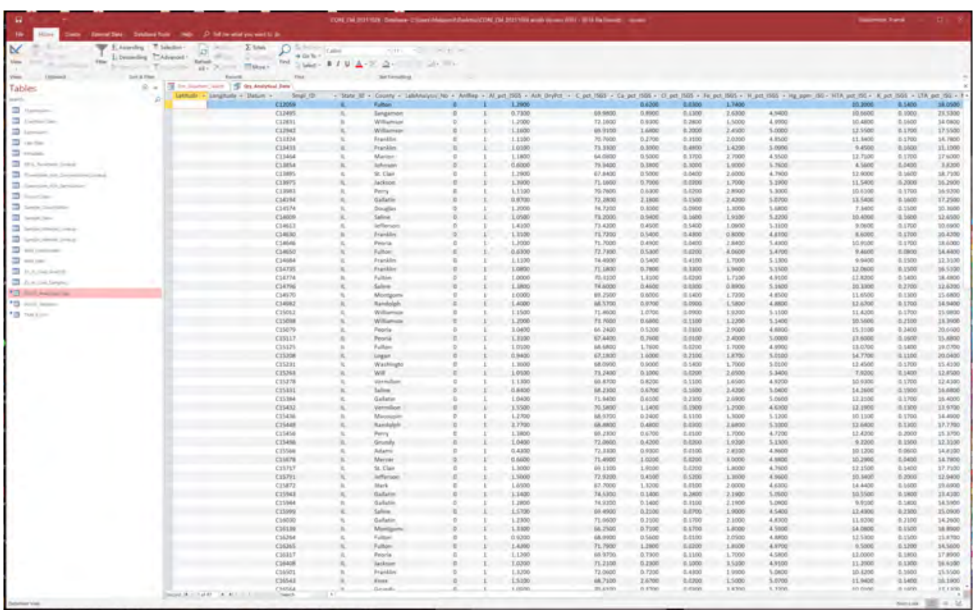


ILLINOIS

Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

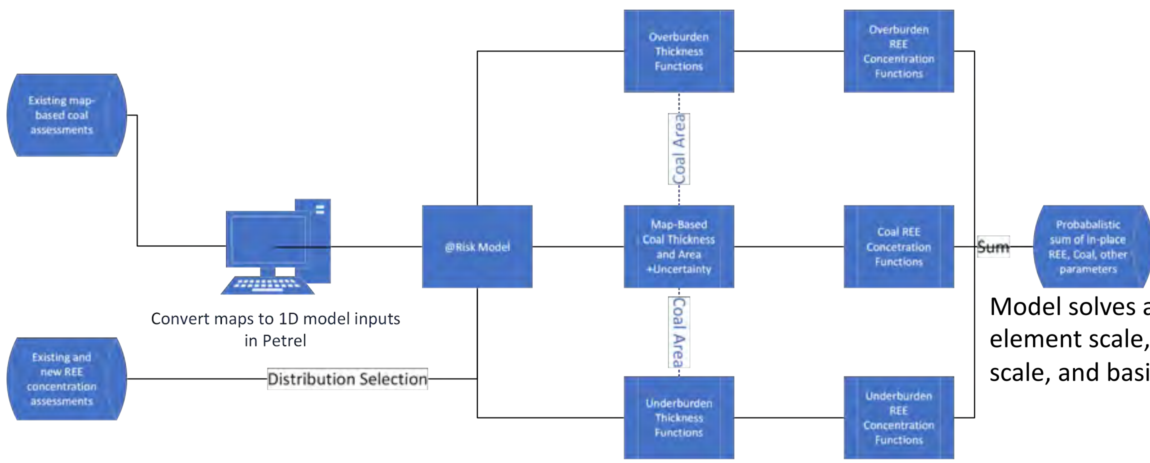
Database Integration, Toolsets, Modeling and Instrumentation



ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Model Design and Volume Equation

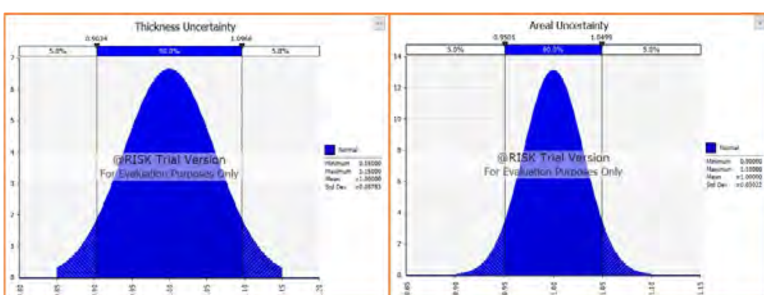
$$\frac{(mass_{coal}\times conc.REE_{ppm\ weight\ basis})+(mass_{country\ rock}\times conc.REE_{ppm\ mass\ basis})}{\sum volume_{coal\ and\ country\ rock}} = \frac{REE\ [sht.tons]}{Volume\ coal\ seam\ [ac\times ft]}$$



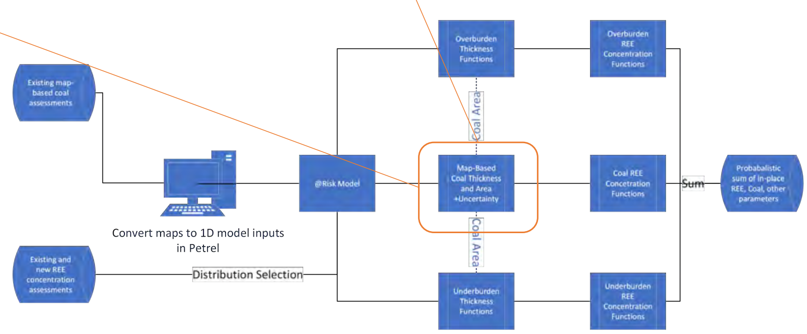
Model solves at small element scale, state scale, and basin scale

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Coal Volume

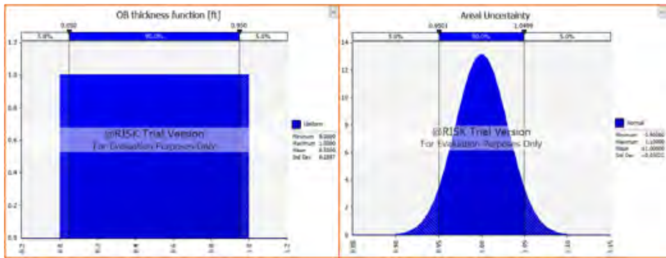


- Areal and thickness uncertainty functions rendered as a modifying factor on map-based results
- In this case:
  - 85% - 115% thickness modifier
  - 90% - 110% area modifier

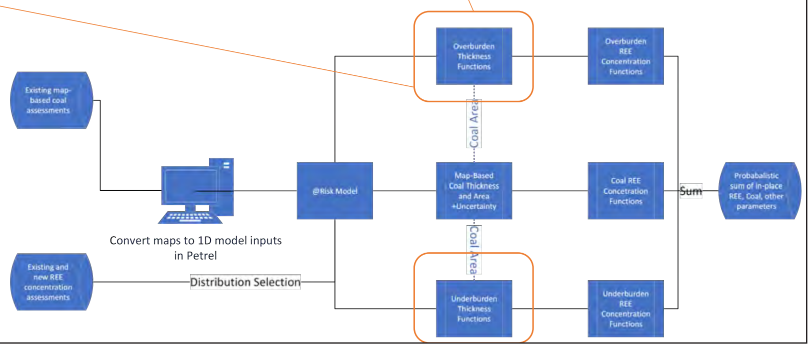


ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Underburden and Overburden Volume

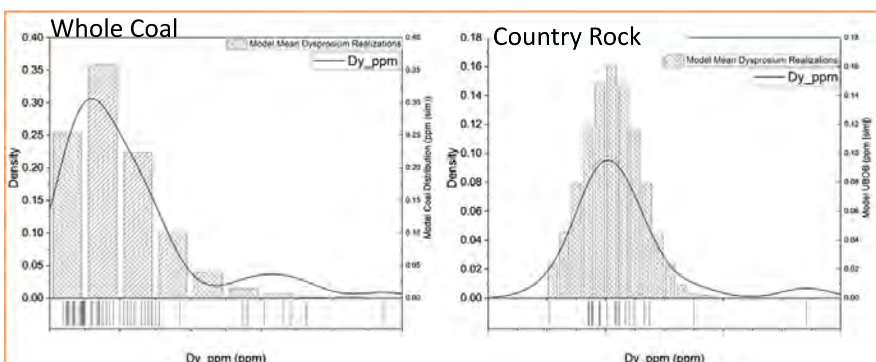


- Underburden and Overburden volume are calculated by a single thickness function applied to the same area that is used for the coal
- In this case:
  - Same area modifier as coal
  - Uniform thickness of 0-1 foot

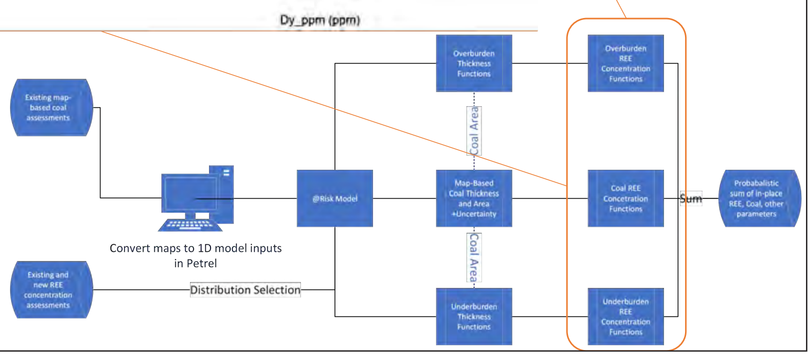


ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

REEs Concentration



- Available analytical data for REE is used to guide concentration function for a given REE
- Example here is Dysprosium
  - Solid black line represents analytical analyses
  - Histogram shows result of Dy concentration distribution in model
- Note that the distribution should capture the **mean** concentration at the scale of the model

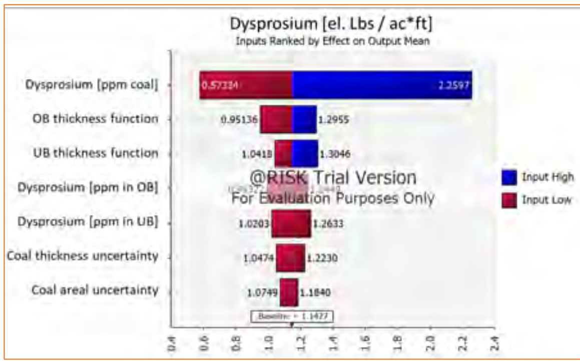


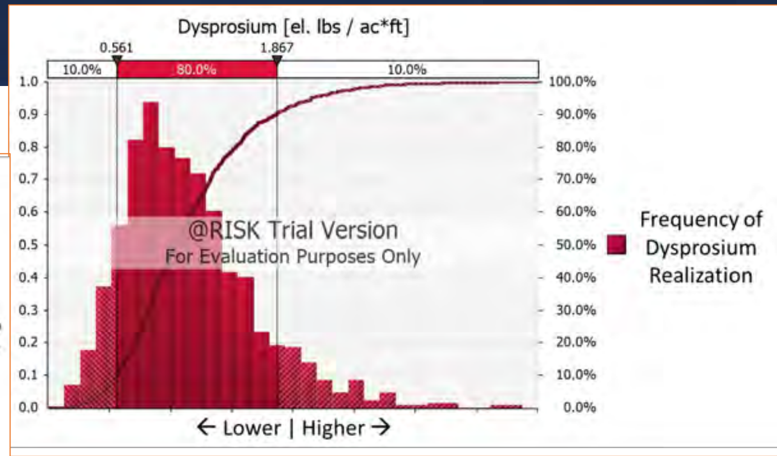
ILLINOIS

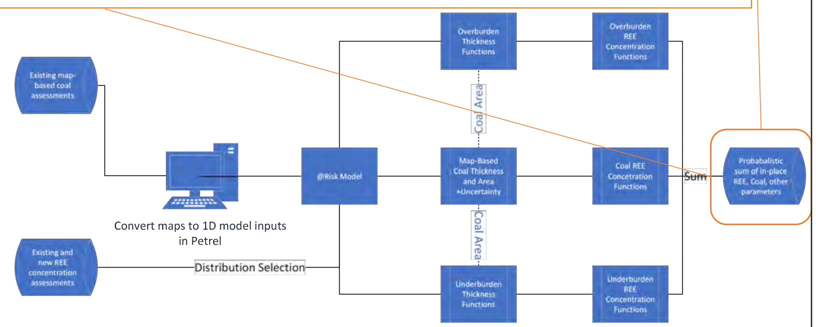
Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

Final Estimate at Model Element Level







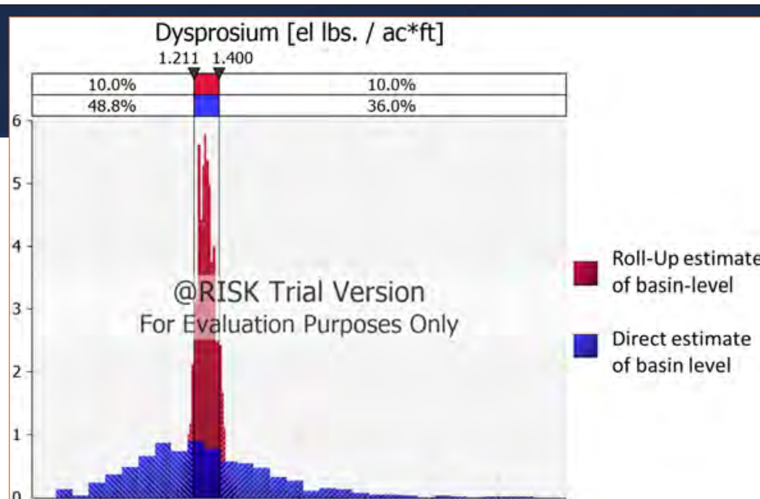
- Result a smallest model element level is similar to the estimates of in-place hydrocarbons
- Model allows transparency through to underlying uncertainty functions

ILLINOIS

Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

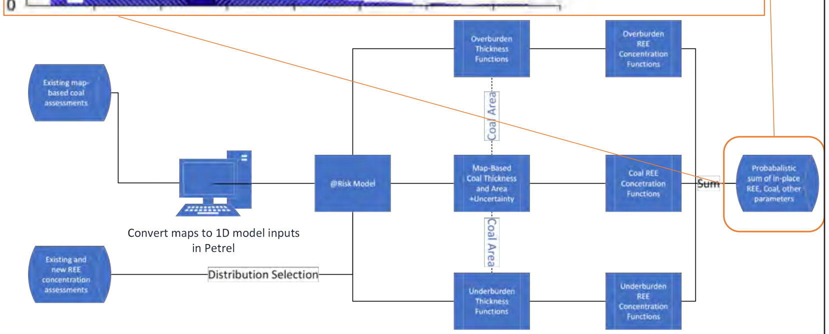
Final Estimate at Model Element Level



- Rollup of granular element estimates (red)
- Direct estimate at the basin scale (blue)

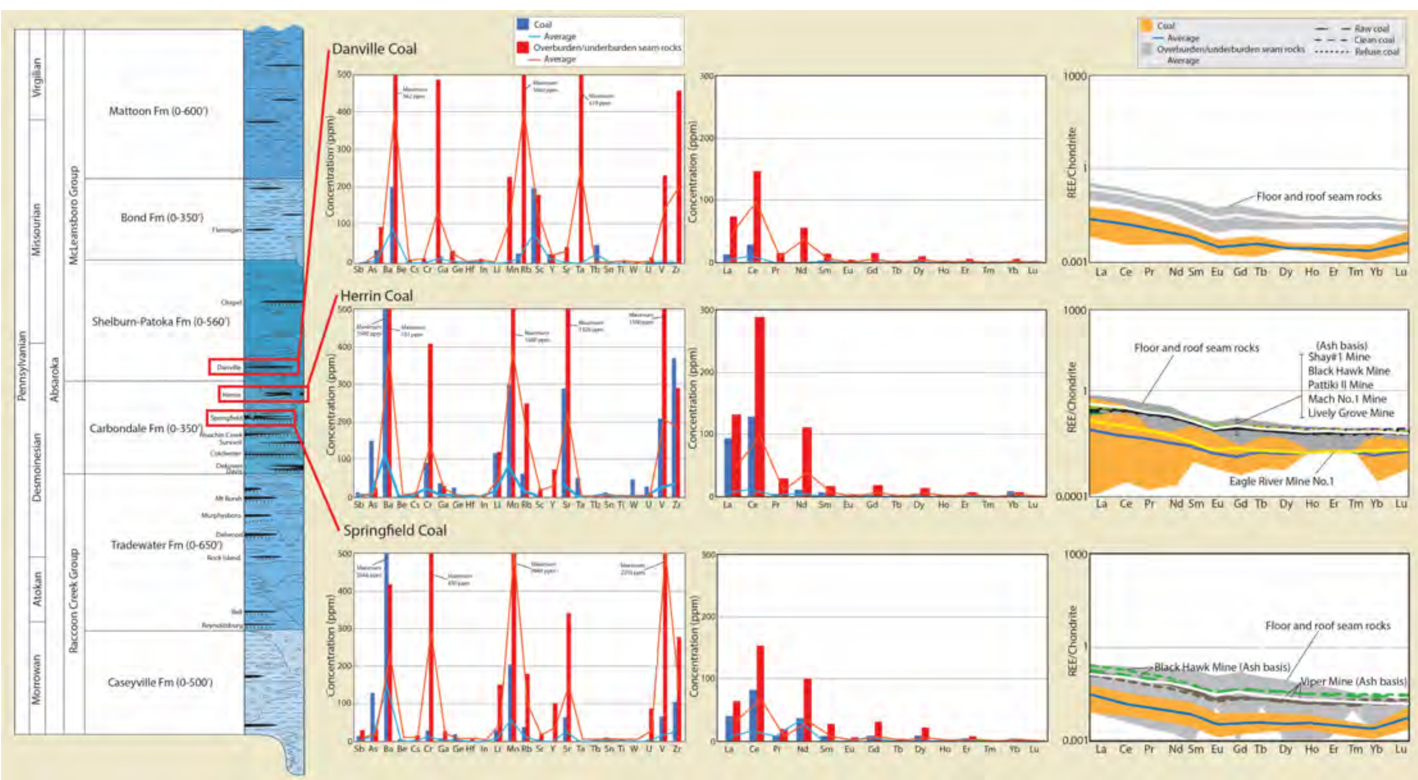
- Rollup has every degree of freedom that the basin scale model has for every element in the model
- This results in an artificially narrow range
- Individual element estimates remain valid
- True range of basin wide resources lies somewhere between these two extremes

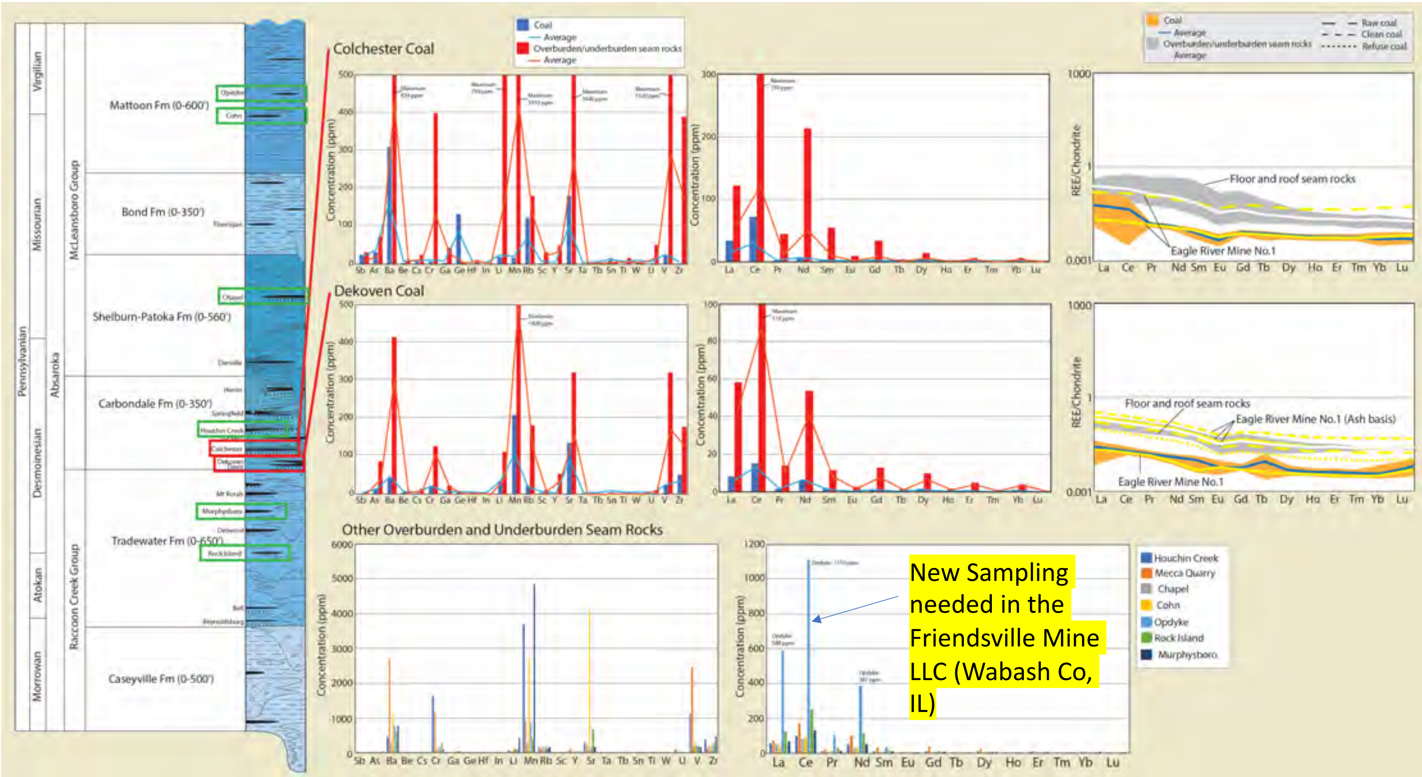
- Correlation parameters may improve spread, some are already applied in model and others are future work



ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Preliminary results



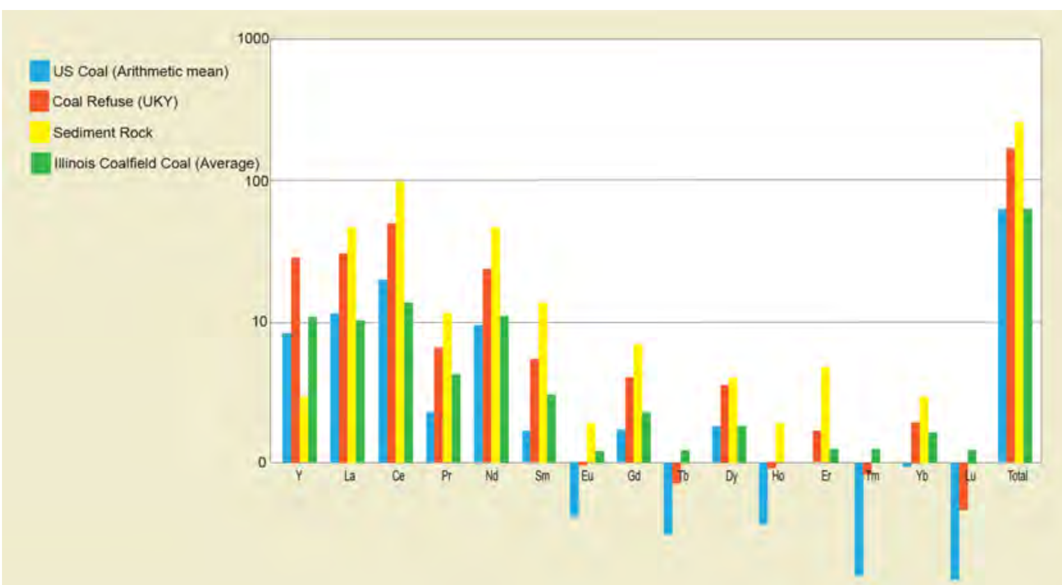


ILLINOIS

Illinois State Geological Survey

PRAIRIE RESEARCH INSTITUTE

REEs Illinois Basin vs REEs U.S. Coal



Source: ILCORECM database and United States Department of Energy Report to Congress (2017)

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Questions?

Illinois Basin CORE-CM

U.S. DEPARTMENT OF ENERGY

Rare Earth Elements and Critical Minerals in Energy-Related Waste Products

Prof. Liliana Lefticariu

Department of Geology, Southern Illinois University, Carbondale, IL

Illinois Basin Carbon Ore, Rare Earth, and Critical Minerals (IB-CORE-CM)

Active coal mines

CMW @ active coal mines included:

- coal refuse that represents materials containing high amounts of mineral matter (ash) that is removed from coal prior to shipment,
- clay/sandstone over/under-burden materials.

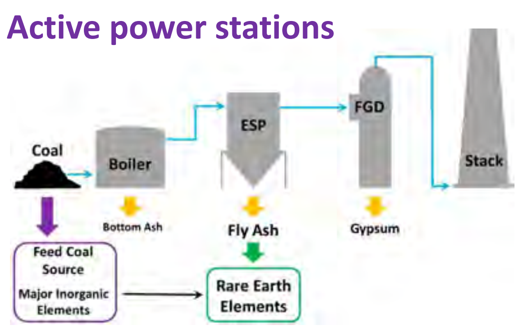
CMW is second only to coal combustion products in terms of REE enrichment

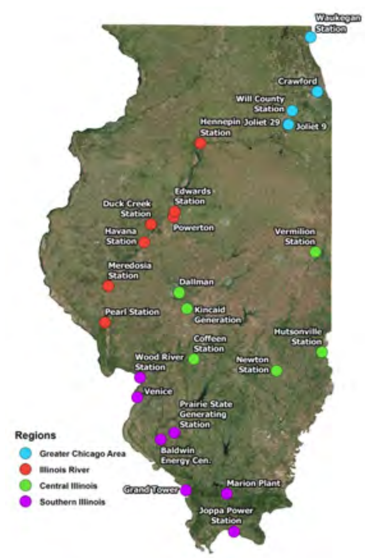
- Samples were collected between 2015 to 2018 and the data were published in USGS Data Series 1135 (https://doi.org/10.3133/ds1135).

Abandoned Mine Lands

- Coal-based acid mine drainage (AMD) includes waters associated with inactive and abandoned coal mining operations, often characterized by high acidity (pH < 5) and elevated concentrations of sulfate (SO4) and metals.
- In addition to AMD, of economic interest are the associated solids (weathering gob piles) and precipitates resulting from AMD treatment.

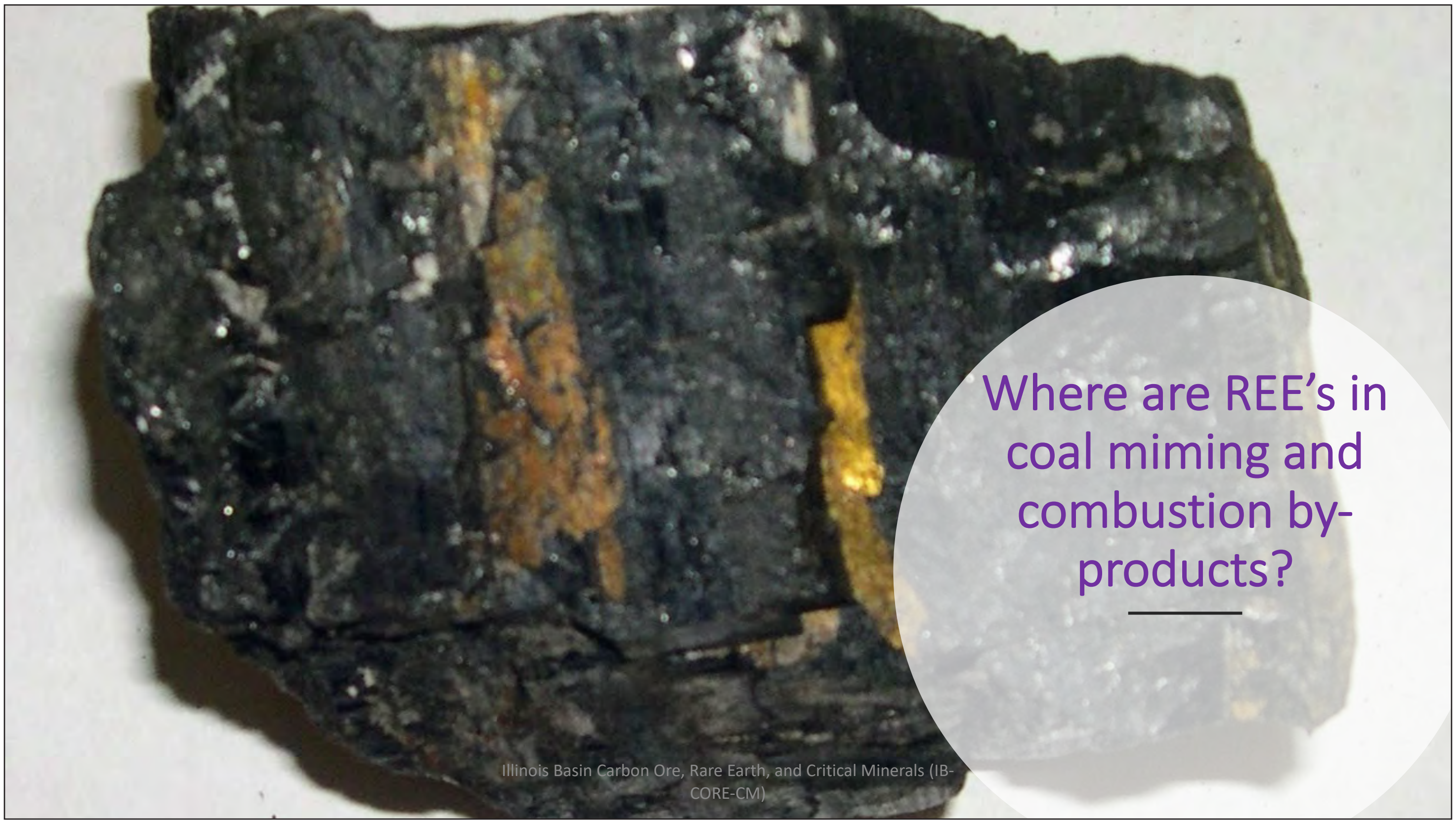
Coal combustion by-products



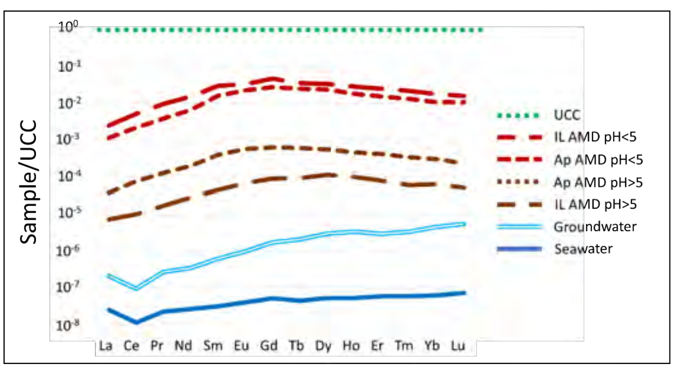


Power stations include:
(1) pulverized coal-fired units (PC units) with wet scrubbers,
(2) fluidized bed combustors, and
(3) institutional and industrial stoker boilers.

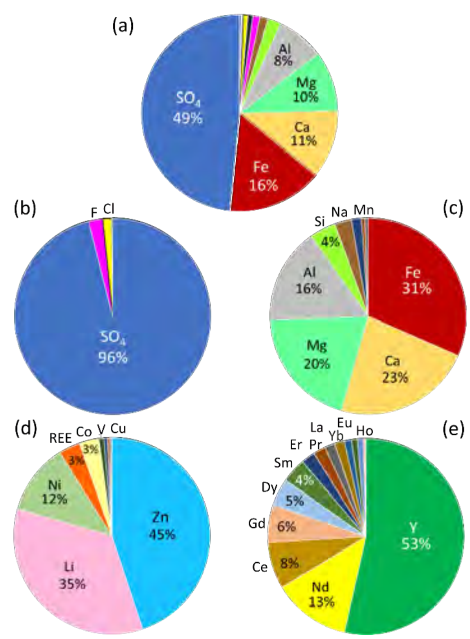
Old coal ash ponds in Illinois can be an environmental hazard if not properly managed.



REEs in Acid Mine Drainage



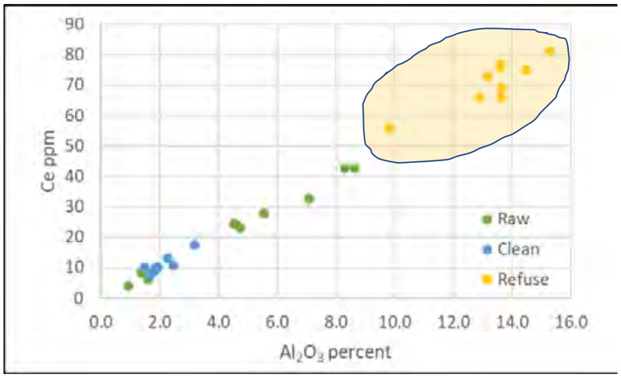
Rare earth element patterns of coal mine drainage (AMD) from the U.S. Appalachian Basin (Ap) and Illinois Basin (IL) normalized to UCC.



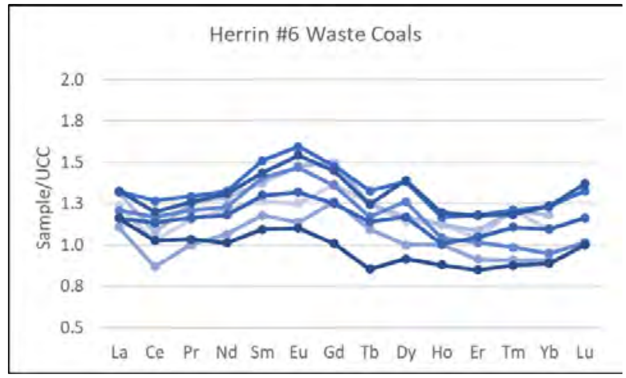
Molal fraction distribution of (a) total ions, (b) major anion, (c) major cation, (d) trace metals and (e) REEs in a typical AMD drainage sample from Tab Simco (Lefticariu et al. (2020)

REEs in Illinois Basin Coals (Active mines)

Herrin #6 Raw, Cleaned and Refuse Coals



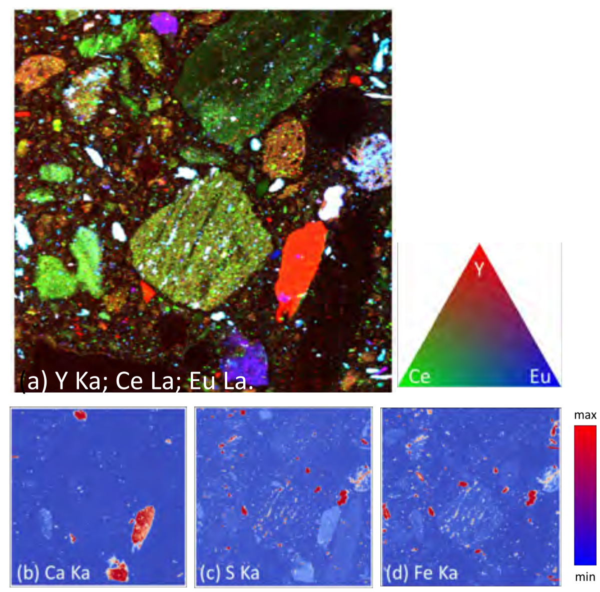
Herrin #6 Refuse Coals/UCC
Raw and Cleaned Coals Not Shown



Kolker, A., Scott, C., Lefticariu, L., Mastalerz, M., Drobniak, A. and Scott, A., 2021. Trace element partitioning during coal preparation: Insights from US Illinois Basin coals. *International Journal of Coal Geology*, p.103781.

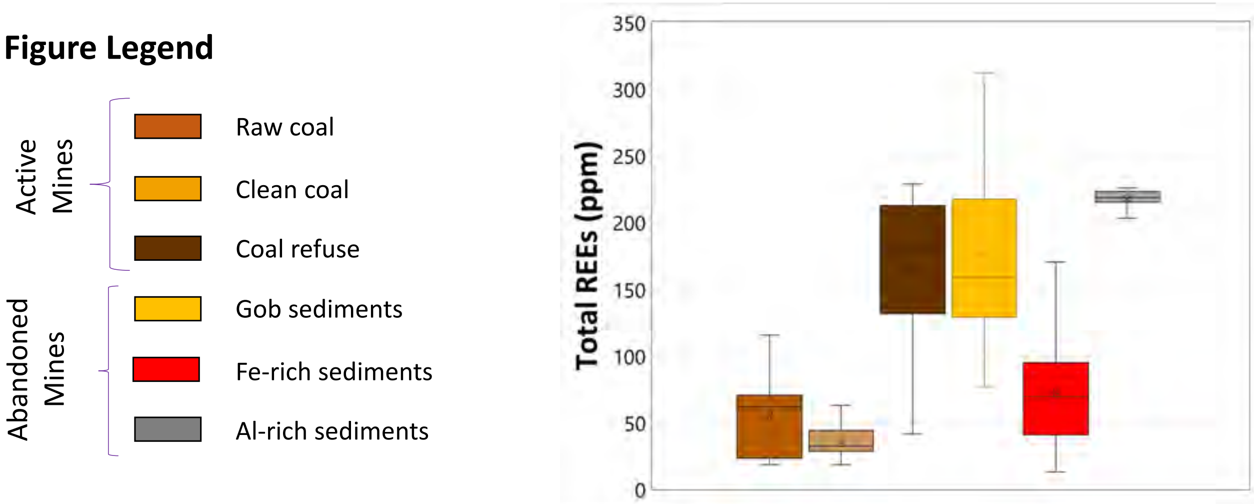
REEs in Coal Mining Waste

- Coal mining waste contains many REE-bearing minerals such as REE-bearing phosphates and REE-bearing silicates. To identify them and provide high-accuracy data at the nanoscale we have employed novel analytical techniques.
- An example is shown in the adjacent figure containing synchrotron µXRF elemental maps showing the distribution of some REE and Ca (proxy for phosphates) and S and Fe (proxy for pyrite).
- The REE-bearing minerals are being targeted in ongoing efforts to recover REEs from CMW.



Synchrotron µXRF elemental maps showing the distribution of some REEs and Ca (proxy for phosphates) and S and Fe (proxy for pyrite). (Lefticariu et al. *in preparation*).

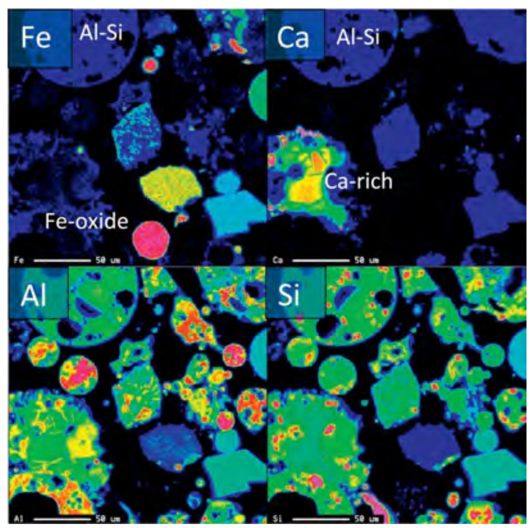
REEs in coal and CMW streams from the Illinois Basin



Illinois Basin: Carbon Ore, Rare Earth and Critical Mineral (CORE-CM)

REEs in coal combustion fly ash

- During coal combustion for electric power generation, rare earth elements (REE) are strongly retained in the ash fraction leading to significant enrichment compared to the REE content of the respective feed coals.
- REE are preferentially partitioned into Al-Si glasses formed at boiler temperatures.
- Ca, Fe-enriched Al-Si glasses have higher REE contents than pure Al-Si glasses.
- REE are present in Fe-oxide magnetospheres in fly ash but are highly depleted in quartz/SiO_2.
- The glass phase should be targeted in ongoing efforts to recover REE from coal fly ash.



Wavelength-dispersive electron microprobe elemental maps for Fe, Al, Ca, and Si of a fly ash sample. Images show Ca-enriched aluminosilicate at center left whose composition is less apparent in the backscattered electron image (Kolker et al., 2017).

REE Distribution in Coal Waste-Related Sources

More

REE concentrations

Less

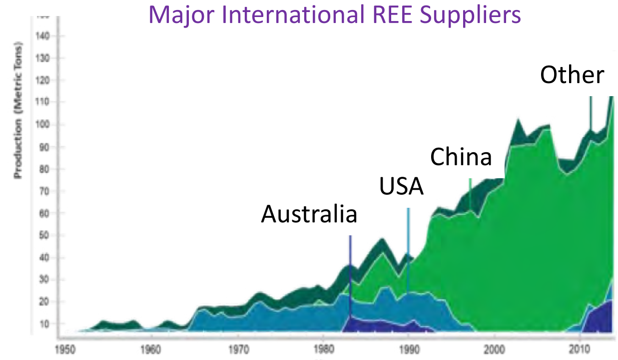
Material	Advantages
Fly Ash	REEs from coal are strongly retained in a smaller mass.
Waste Coal	Non-coal material is REE-enriched relative to coal itself.
Raw Coal	Abundant and well understood.
Acid Mine Drainage	REEs already in solution or in a colloidal form.

Illinois Basin Carbon Ore, Rare Earth, and Critical Minerals (IB-CORE-CM)

Introduction

- The United States is dependent on China and other offshore sources for numerous critical materials that are essential U.S. economy and national security.
- These include rare earth elements (REEs), and other critical minerals (CMs).
- A strategic priority is to resource the production of REEs and CMs and their associated supply chains back to the U.S. as evidenced by recent and proposed legislation as well as by several Executive Orders, including the President's recent declaration that the CM supply chain is a national emergency.

Major International REE Suppliers



https://netl.doe.gov/coal/rare-earth-elemgroents/program-overview/backund

- Consequently, research, development and demonstration (RD&D) efforts to create new domestic sources of REEs and CMs have been accelerated with the national goal of making our domestic supply chains more resilient.

Illinois Basin Carbon Ore, Rare Earth, and Critical Minerals (IB-CORE-CM)

Questions?

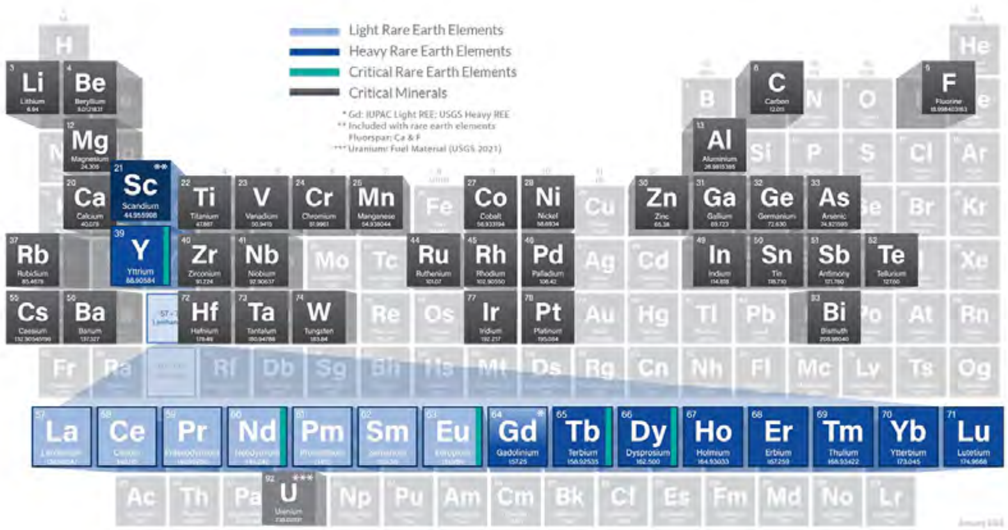
Critical minerals (CMs) and Rare earth elements (REEs)

- Critical minerals (CMs) were defined by the Energy Act of 2020 as a non-fuel mineral or mineral material essential to the economic or national security of the U.S. and which has a supply chain vulnerable to disruption.
- Critical minerals are also characterized as serving an essential function in the manufacturing of a product, the absence of which would have significant consequences for the economy or national security.
- Rare earth elements (REEs), which are part of CMs, are a group of 16 elements comprising the lanthanides, yttrium, and scandium that exhibit similar physicochemical characteristics and tend to co-occur in nature.

Illinois Basin Carbon Ore, Rare Earth, and Critical Minerals (IB-CORE-CM)

Critical Minerals Including Rare Earth Elements

Source: The [2022 list of critical minerals](#) compiled by USGS.



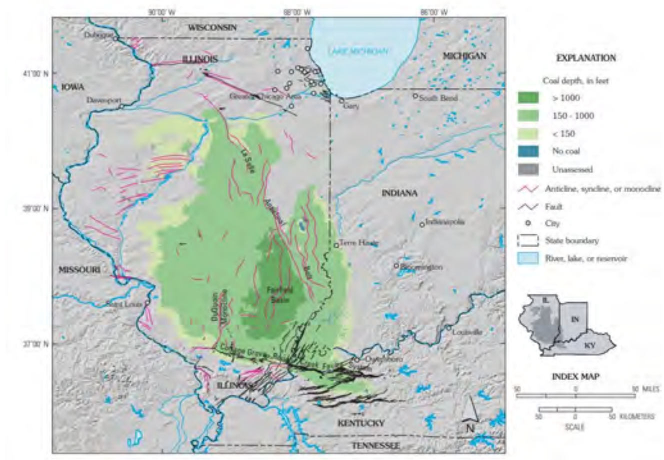
Critical Elements in Coal Waste Streams

In terms of economic significance, two main groups of elements are relevant to this research.

- **Lithophile elements** includes REEs, Li, Al, P, Ti, Rb, Zr, Nb, Cs, Ba, Hf, Th, and U. Many of these elements belong to CMs group, and thus have high economic value.
- **Chalcophile elements** includes Fe, S, Zn, As, Sb, Hg, and Pb. This group of elements, hosted primarily by pyrite and other sulfide minerals are also enriched in CMW. These elements have high toxicity potential and are of environmental concern when affecting natural soil and water resources.

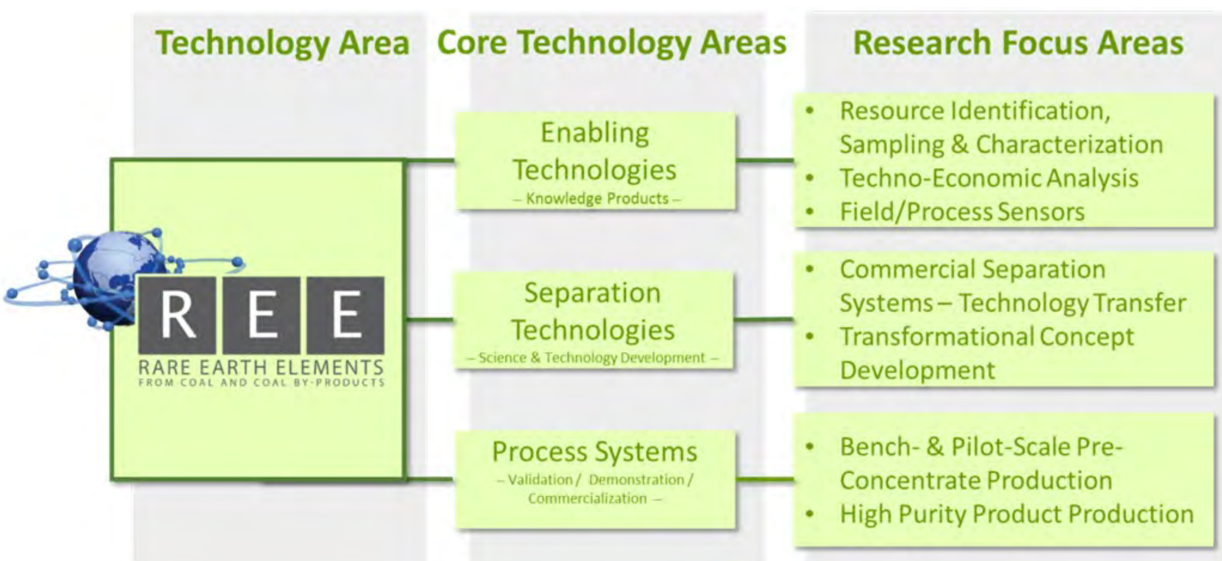
Illinois Basin CORE-CM Initiative Resource Assessment

- To address the challenge of leading U.S. to secure national independence from CM offshore reliance, the Department of Energy (DOE), Office of Fossil Energy (FE) and the National Energy Technology Laboratory (NETL) have been sponsoring a wide rage of research projects, including the ***IB-CORE-CM project***.
- One important goal has been to assess the potential recovery of REEs and other CMs from coal and coal by-products. These materials show relative enrichment in REEs and other lithophile elements compared to as-mined or prepared coal but are also enriched in chalcophile elements such as Hg, Pb, and As, as pyrite is reduced in clean coal during coal preparation.
- Recovery of REEs from coal waste products is one of the more promising approaches to REE recovery. Use of coal waste products to extract REE helps reduce the impact of this waste.



Illinois Basin Carbon Ore, Rare Earth, and Critical Minerals (IB-CORE-CM)

Recovery of REEs from coal-based resources



https://netl.doe.gov/coal/rare-earth-elemgroents/program-overview/backund

Study Approach

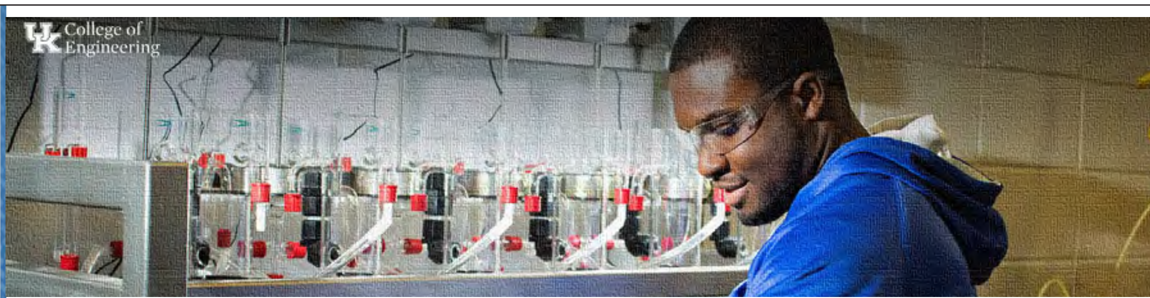
- To better understand the distribution of REEs and other CMs in coal mining waste streams and their behavior during weathering, we analyzed samples collected at both active and abandoned coal mining operations in the Illinois Basin.
- Samples collected at:
  - **(1) <u>Active coal mines</u>:**
    - Coal mine waste (CMW) newly generated coal refuse from mining and coal preparation
    - Raw (as mine) coal
    - CleanED coal
  - **(2) <u>Abandoned coal mines:</u>**
    - Acid mine drainage (AMD)
    - Weathered coal mining waste (i.e., gob piles)
    - Fe-sediments associated with acid mine drainage (AMD)
    - Al-rich sediments collected from passive bioreactors

Illinois Basin: Carbon Ore, Rare Earth and Critical Mineral (CORE-CM)

REEs host minerals

- Common REEs-bearing minerals include:
- REEs-bearing phosphates:
  - Monazite or its hydrated equivalent, Rhabdophane $(REE)PO_4*H_2O$
  - Xenotime $(Y)PO_4$
  - Apatite $Ca_5(PO_4)_3(OH,F,Cl)$, and
  - Crandallite $(CaAl_3(PO_{3.5}(OH)_{0.5})_2(OH)_6$
- REEs-bearing silicates:
  - Allanite $Ca(REE)Al_2Fe^{2+}[Si_2O_7][SiO_4]O(OH)$,
  - Zircon $(ZrSiO_4)$
- REE-rich clays (i.e., REEs adsorption on clays)

Mineral	Formula
	Oxides
Aeschynite	$(Ce,Th,Ca...)[(Ti,Nb,Ta)_2O_6]$
Euxenite	$(Y,Er,Ce,U,Pb,Ca)(Nb,Ta,Ti)_2(O,OH)_6$
Fergusonite	$YnbO_4$
Samarskite	$(Y,Er,Fe,Mn,Ca,U,Th,Zr)(Nb,Ta)_2(O,OH)_6$
	Carbonates
Ancylite	$Sr(Ce,La)(CO_3)_2(OH)\cdot(H_2O)$
Bastnasite	$(Ce, La,Y)CO_3F$
Parisite	$Ca(Ce,La)_2(CO_3)_3F_2$
Synchisite	$Ca(Ce,Nd,Y,La)(CO_3)_2F$
Tengerite	$Y_2(CO_3)_3{\bullet}n(H_2O)$
	Phosphates
Britholite	$(Na,Ce,Ca)_5(OH)[(P,Si)O_4]_3$
Florencite	$(La,Ce)Al_3(PO_4)_2(OH)_6$
Monazite	$(Ce,La,Th,Nd,Y)PO_4$
Xenotime	YPO_4
	Silicates
Allanite	$Ca(Ce,La,Y,Ca)Al_2(Fe^{2+},Fe^{3+})(SiO_4)(Si_2O_7)O(OH)$
Kainosite	$Ca_2(Ce,Y)_2(SiO_4)_3CO_3\cdot H_2O$
Thalenite	$Y_2[Si_2O_7]$



REE Separation Technologies from Coal and Coal Waste in the Illinois Basin

R. Honaker
Department of Mining Engineering
University of Kentucky

Illinois Basin Critical Minerals Short Course
Eastern Section American Association of Petroleum Geologists
October 26, 2022

Associated Mineral Advantage

- Coal is associated with minerals that provide natural acidity and alkalinity:
  - Pyrite
  - Calcite
- Both minerals have physical properties that allow low cost recovery and concentration.

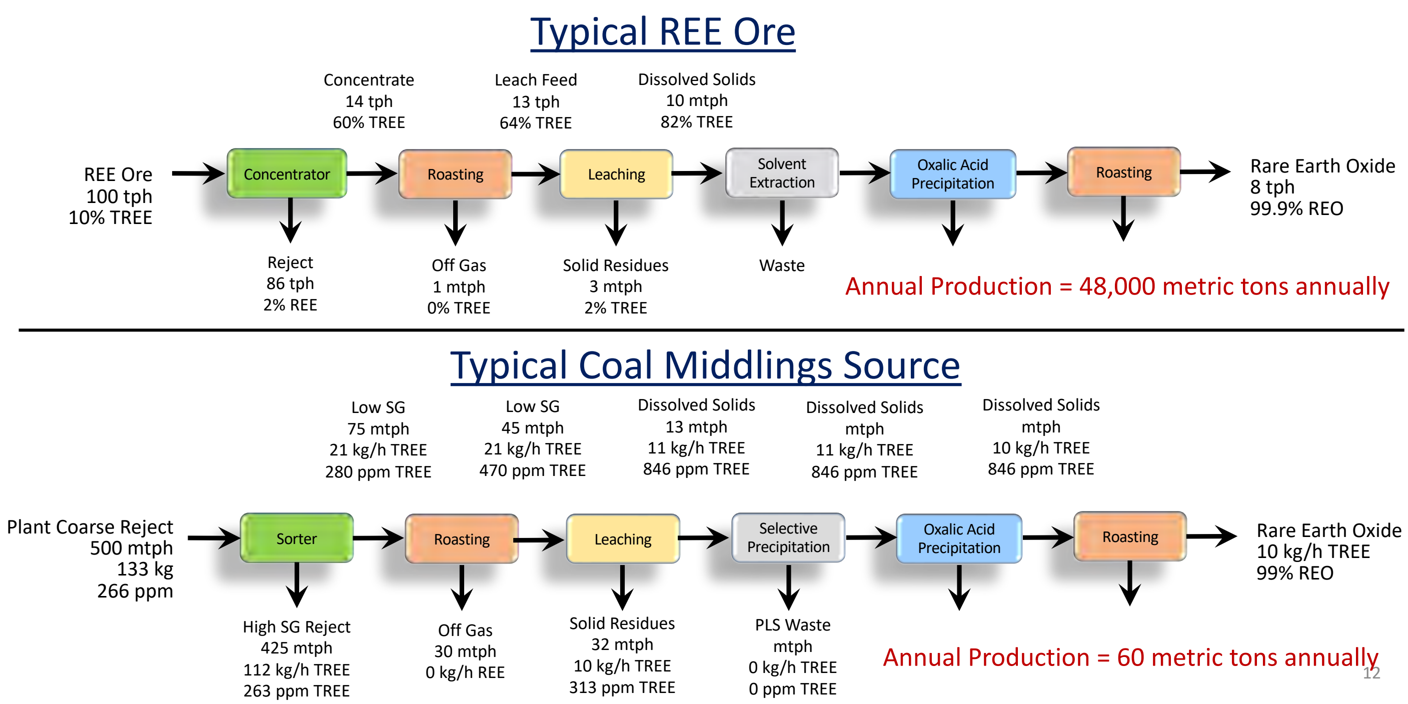
Size Fraction (mesh)	Weight (%)	Major Minerals (%)			
		Pyrite	Silica	Calcite	Kaolinite
+100	8.84	6.3	6.4	68.2	4.9
100 x 200	43.72	20.0	14.1	62.8	3.1
200 x 325	14.88	43.3	12.2	35.4	1.1
-325	32.56	30.1	44.8	21.0	3.7
Total	**100.00**	**25.5**	**23.1**	**45.6**	**3.2**

10

Bioreactor: Sulfuric Acid Production

- Two 3000-gallon bioreactors were equipped with Denver sub-aeration units (40 hp), 8-ton chilling capacity and a blower.
- Pyrite (60%+ grade) slurry was added at a 5% solids from a 3000-gal tank.
- *Acidithiobacilus ferrooxidans* was added to aid the iron oxidation process.
- Production of sulfuric acid has been 300 gallons daily for a single reactor.
- Bioacid with a pH of around 0.7 and an effective concentration of 0.5 M has been generated.

Block Flow Diagram Comparison

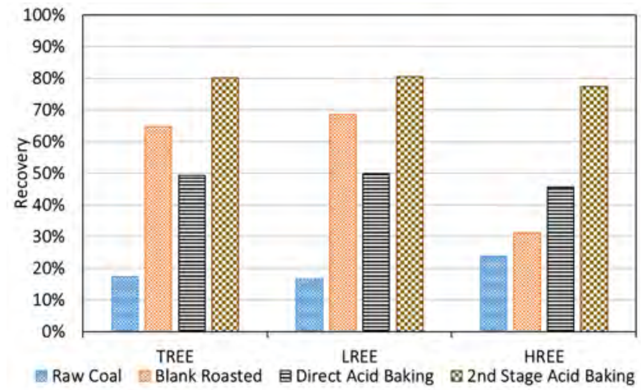


12

Pre-Treatment Options for Tank Leaching

- Calcination (roasting) at 600^{O}C improves light REE recovery due to the decomposition of crandallite-group minerals.
- Acid baking decomposes xenotime and zircon to elevated heavy REE recovery.
- Relatively expensive option despite the high REE recovery (acid-to-solids ratio = 1:1).
- Lynas is installing a 110 meter long Metso rotary tube roaster valued at $15 million.

Baker Coarse Refuse



13

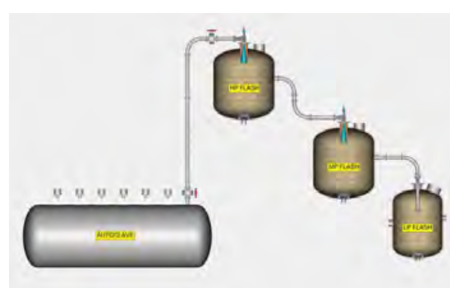
Leaching Options

- Leaching involves solubilizing a desired mineral to recover a target element using a given lixiviant under a desired temperature and pressure.
- Typical lixiviants include sulfuric, hydrochloric and nitric acids. Sulfuric is most common (cost).
- As such, heap leach is preferred as a 'cheap' option to minimize cost.
- Tank leaching is common for high grade sources.
- High Pressure Acid Leach (HPAL) is a process used to extract nickel and cobalt from laterite ore bodies; temperature = 255^{O}C, pressure = 725 psi, and sulfuric acid.

Acid Leach Tank

Heap Leaching

High Pressure Acid Leaching



https://www.calderaengineering.com

Selective REE Bioleaching

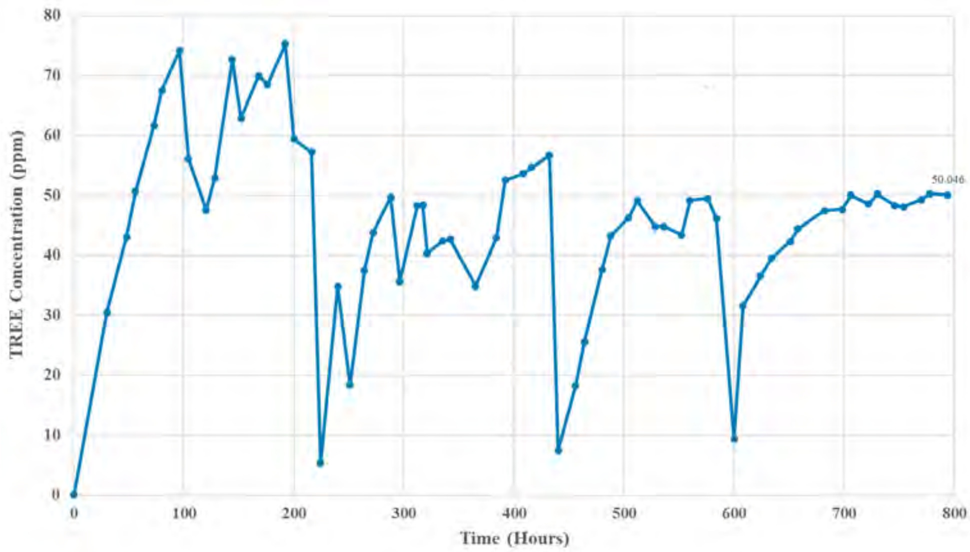
- Bioleaching has the potential to selectively extract REEs and other critical elements directly from the solids and avoid/minimize contaminant recovery.
- Biomolecules called lanthanomes bind, transport and employ REEs.
- The lanthanomes survive due to the presence of REEs to serve as a catalyst for methane oxidation to methanol to CO_2. Methane is the primary energy source.

Heap Leach Test Pad

- 2000 tons of Baker (West Kentucky No. 13) seam coarse coal refuse
- 65 x 65 square feet heap leach area with a 15-ft vertical lift
- Underlined with a clay liner and a HDPE 60 mil liner
- Surrounding berm constructed based on a 100-yr rain event
- Sump to collect 3000 gallons of the pregnant leach solution (PLS)
- A 5000 gallon PLS storage tank and four 5000 gallon tanks for rain event water storage

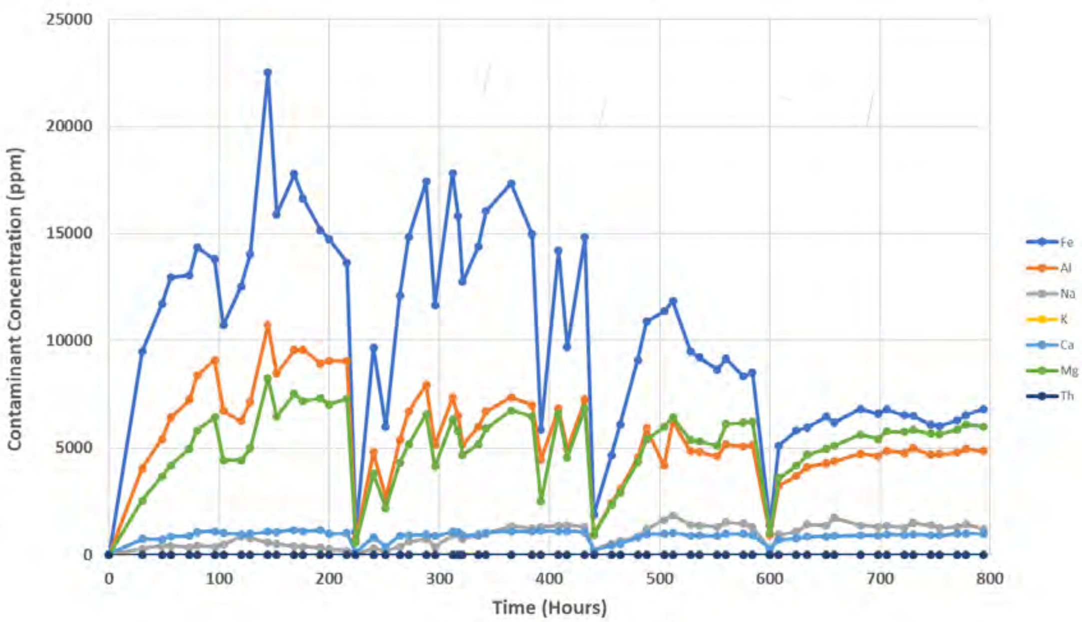
16

Heap Leach REE Content in Pregnant Leach Solution



17

Heap Leach Contaminant Leaching Performance

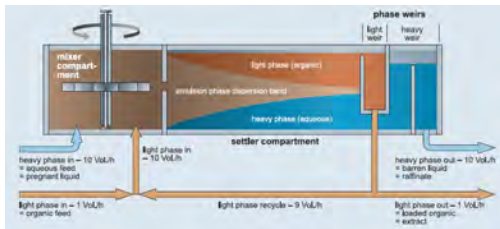


18

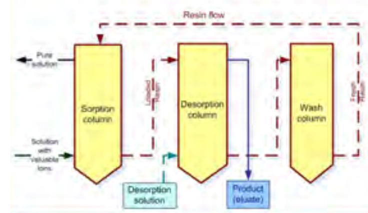
Rare Earth & Critical Material Purification Technologies

- SX is the most widely used technology
  - Requires 900 – 1000 mixer settlers to produce 16 individual REE products.
  - Environmental concerns
- Ion exchange is an alternative
- Emerging technologies:
  - Ion Chromatography
  - Membrane Separation
  - Molecular Recognition
  - Biofilm
  - Microbial Encapsulation

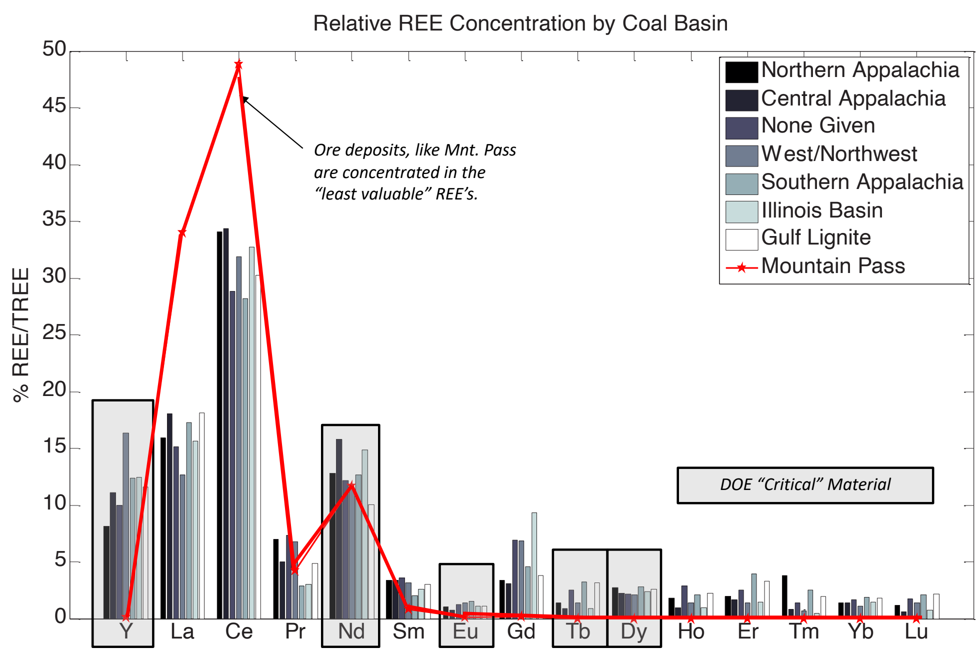
Solvent Extraction (SX)



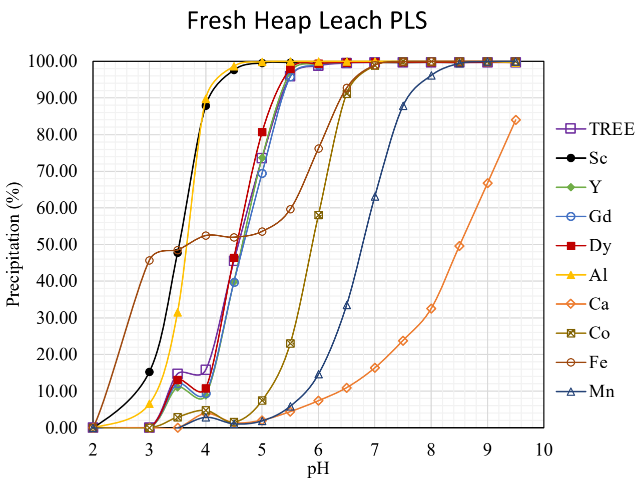
Ion Exchange (IX)

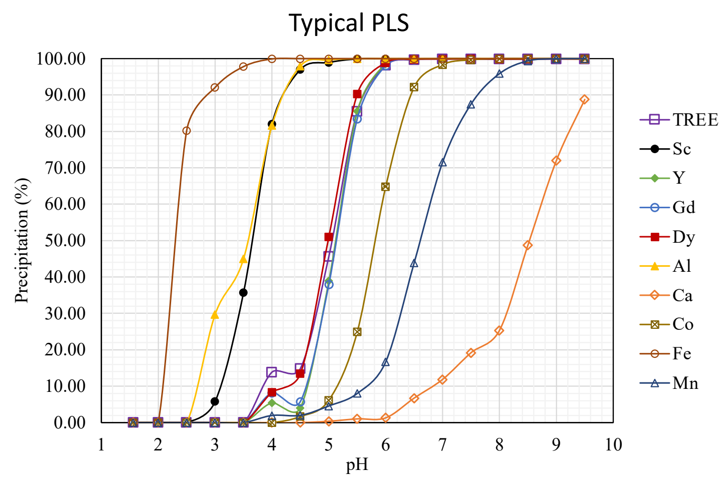


Coal-based vs. Mountain Pass REE Distribution



Coal-Based Selective Precipitation Performance

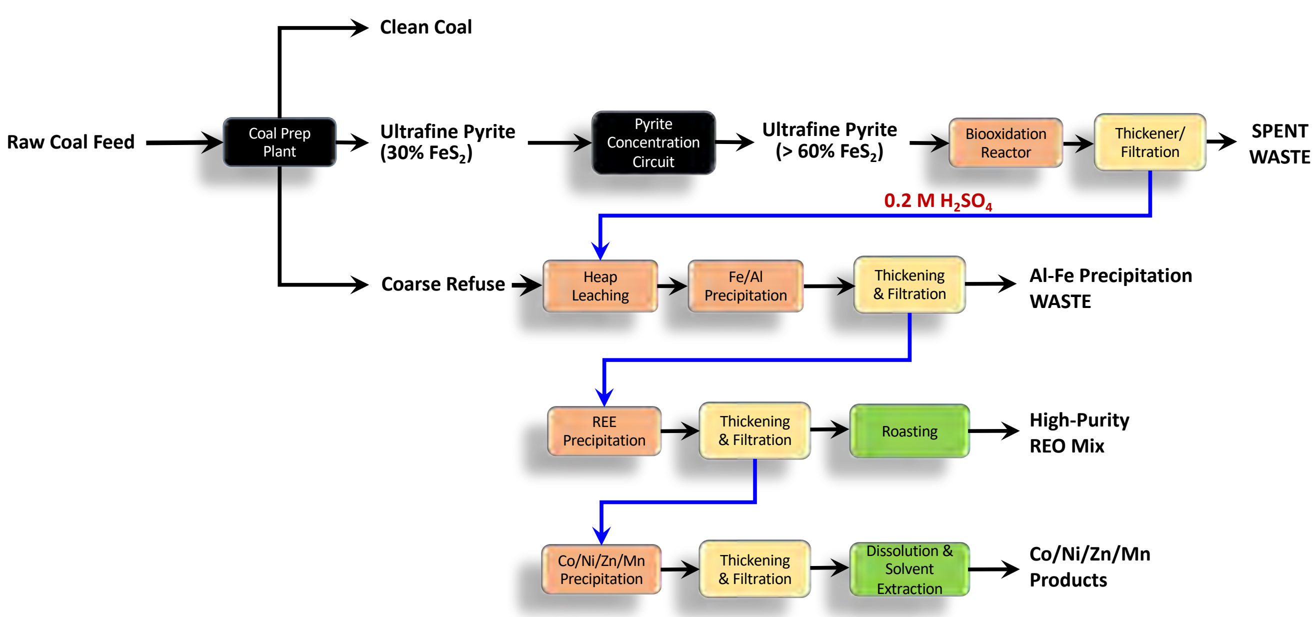




- Staged precipitation can effectively remove Fe^{3+} and Al while concentrating REEs and other critical metals.
- The natural heap PLS contains a significant amount of Fe^{2+} which starts precipitating at pH 5.5 thereby requiring a step to oxidize ferrous to ferric potentially by biooxidixation.

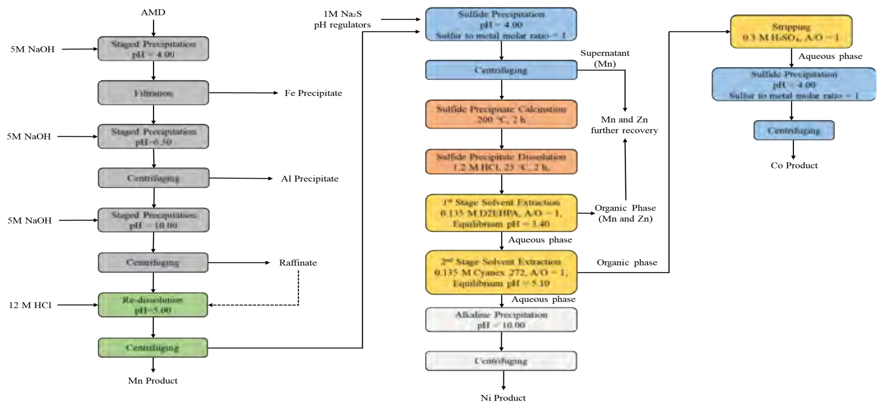
20

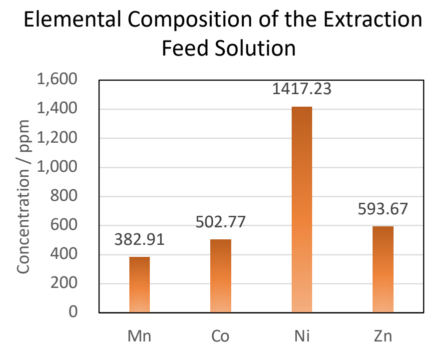
Block Flow Diagram for Heap Leach PLS Treatment



21

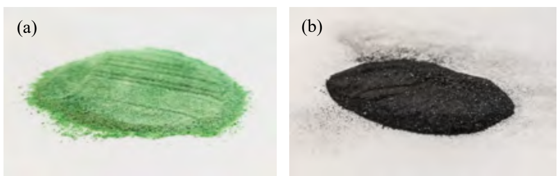
Co/Ni/Co/Mn Processing

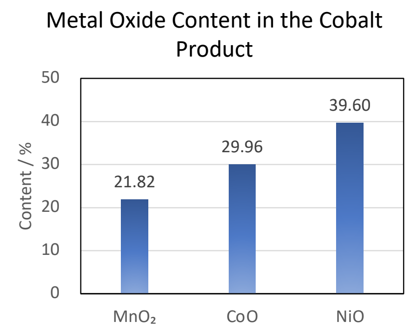




NiO = 96.2%

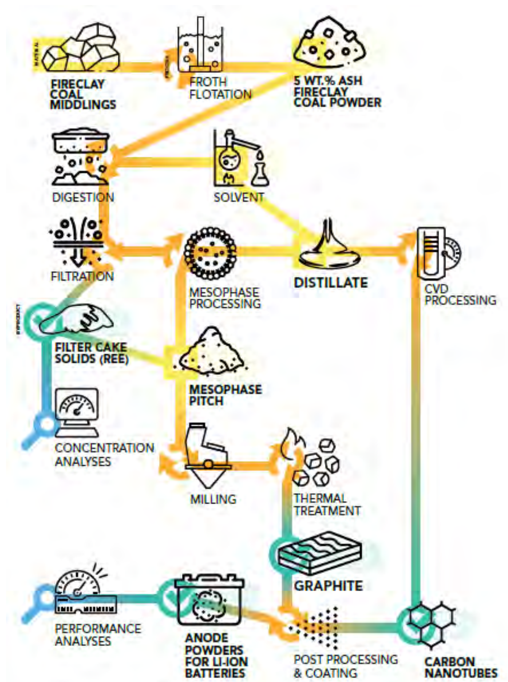
CoS = 98.0%





Economic Commercial Potential

- Middling fractions of coal sources have REE and CM that are associated with minerals having a lower degree of crystallinity.
- As a result, the REEs and CMs are more easily leached using weaker acid solutions.
- Lower contaminant contents.
- Associated coal can be processed to produce multiple high-value products.
- Multiple products greatly benefits economic potential.



Summary

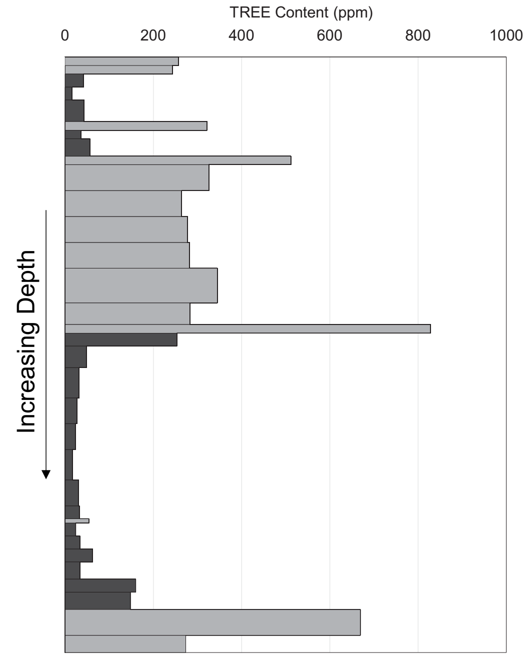
- Coal-based materials have an attractive distribution of REEs and other critical elements like Co, Ni and Ge.
- The most common REE mineral found in Illinois Basin coal are crandallite-group minerals.
- Grain size limits physical concentration.
- Pre-leach roasting assists recovery.
- Naturally occurring minerals in coal could be beneficial for extraction.
- Selective leaching technologies and purification systems for dilute and dirty PLS would benefit recovery from coal sources.

REE Forms in Coal

- Mineral association
  - monazite $(Ce,La,Pr,Nd,Th,Y)PO_4$
  - crandallite $(CaAl_3(PO_4)_2(OH)_5 \bullet (H_2O))$
  - xenotime (YPO_4)
  - bastnaesite $(Ce, La)CO_3F$
  - zircon $ZrSiO_4$, $(Zr_{1-y}, REE_y)(SiO_4)_{1-x}(OH)_{4x-y}$
  - apatite $Ca_{10}(PO_4)_6(OH,F,Cl)_2$
- Ion substitution in clay
- Organic association

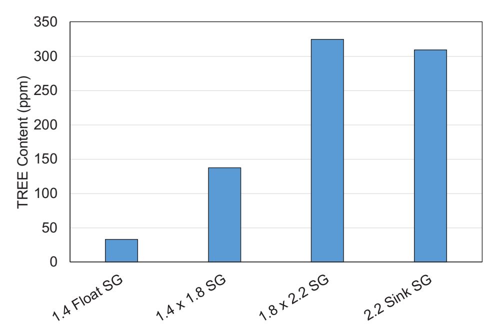
Stratigraphic Analysis

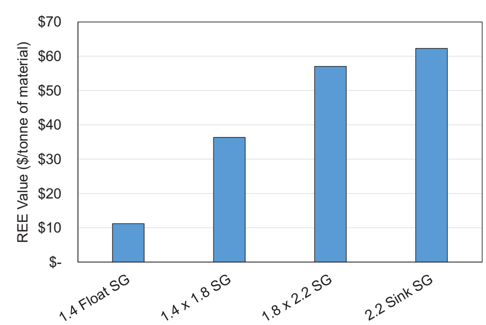
- Detailed stratigraphic studies on cores samples have been conducted on numerous coal sources including the Baker seam in western Kentucky.
- Some lithologies contain significant concentrations of REEs, as high as 830 ppm.
- Approximately 40% of the Baker seam thickness approaches or exceeds 300 ppm, which is a threshold value for many DOE studies.



Distribution of REEs and Values by Density

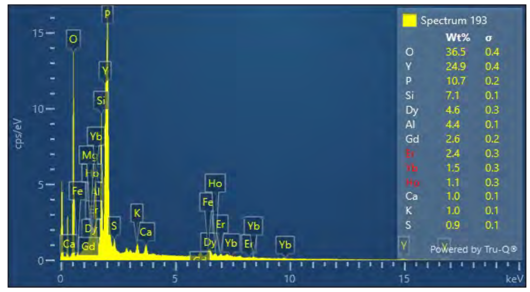
- Density fractionated material from the plant feed (indicative of the bulk product from the prep plant) show good correlation to the stratigraphic data.
- High density material in the 1.8 x 2.2 and 2.2 sink fractions contain about $55 to $60 of REEs per tonne of material.
- Assuming a coarse refuse production rate of 648 TPH and 6000 hours per year, this totals to <u>**$211 million per year**</u> of REEs going to the coarse refuse pile.

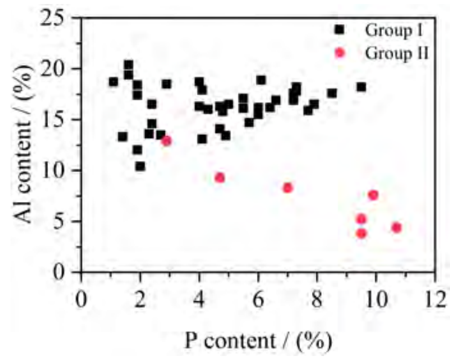




SEM-EDAX Analysis

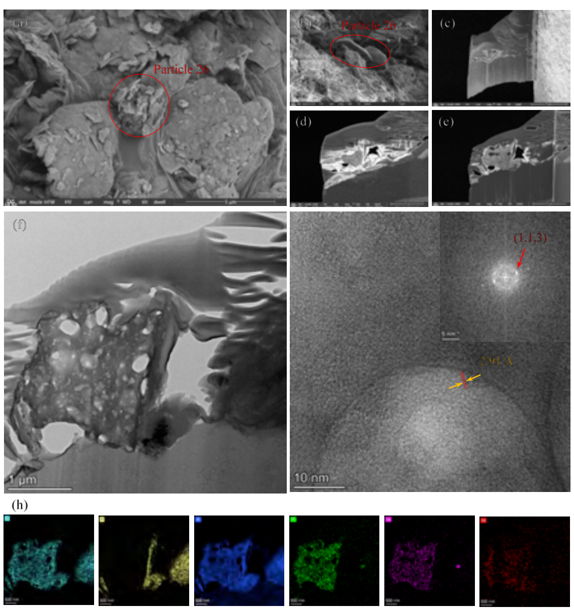
- Study was conducted on coarse refuse generated from the Baker seam.
- Most particles showed relatively high contents of Ca, Sr, and Ba, agreeing with the chemical formula of crandallite-group minerals.
- The REEs in zircon and xenotime were primarily heavy REEs.
- REEs in apatite were primarily light REEs.

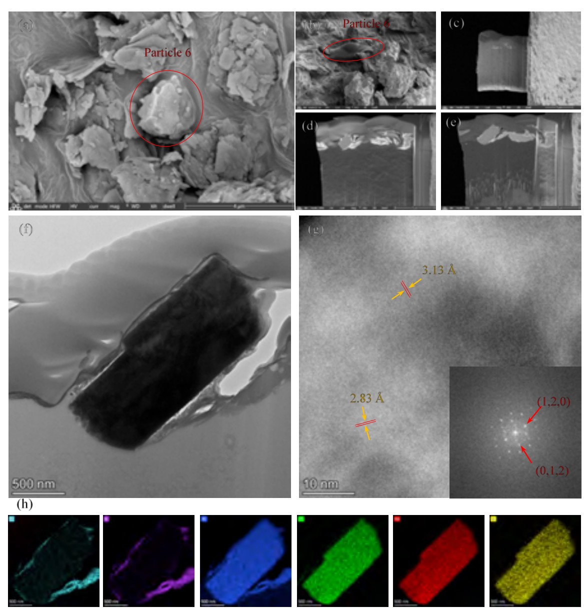




REE Mineral Grain Size

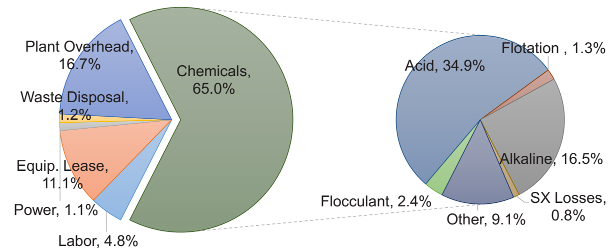
Grain size is less than 10 microns and most are less than 1 micron.





Processing and Economic Challenges

- REE mineral grain size is less than 10 microns which limits the ability to pre-concentrate like other richer REE deposits.
- Requires direct hydrometallurgical processing which leads to high contamination in the pregnant leach solution.
- Low feed grade, poor leaching recovery, low PLS concentration, and waste disposal are other concerns of note.
- Prior analyses have shown that chemical costs (acid and base) are a major impediment to an economically viable process.

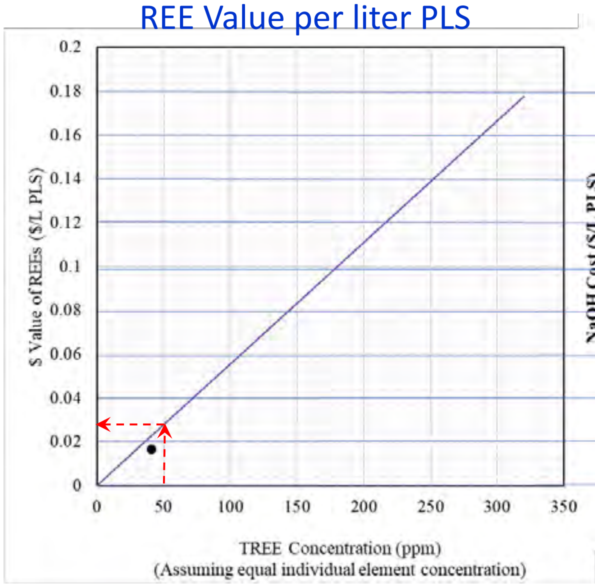


OPEX breakdown for a hypothetical coal-based REE recovery facility.

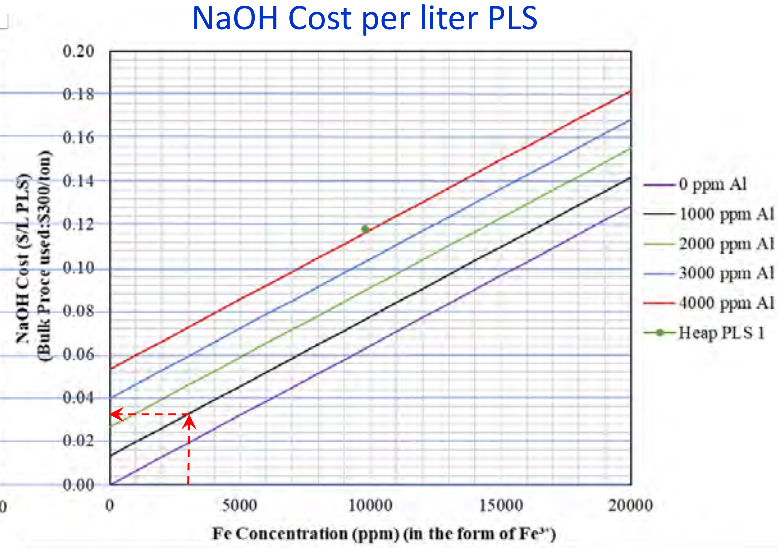
8

Simple Base Cost Analysis:
Strong acid conditions needed to leach the identified REE minerals which required base to neutralize

REE Value per liter PLS



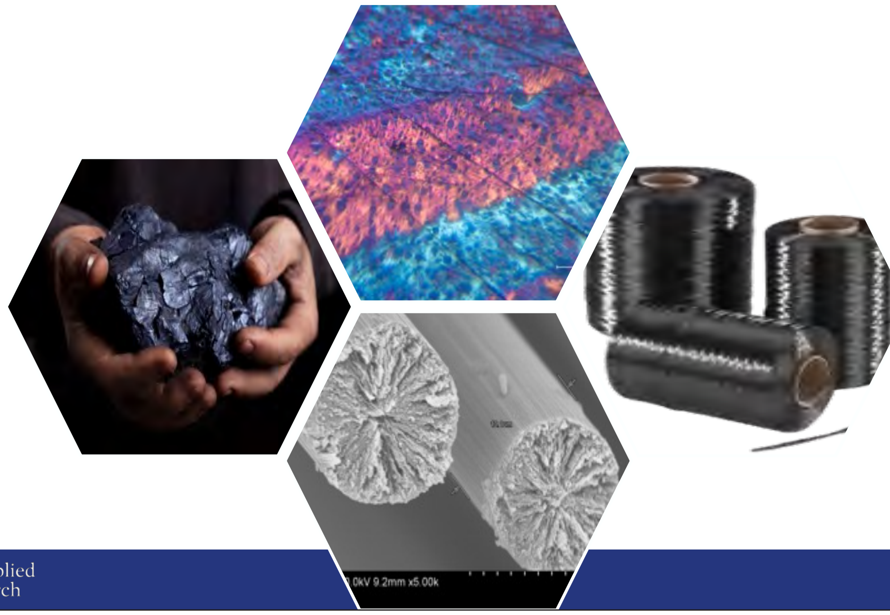
NaOH Cost per liter PLS



Example: 50 ppm REE value = 0.028 $/liter

3000 ppm Fe & 1000 ppm Al = 0.032 $/liter NaOH cost

Advanced Carbon Products from Illinois Basin coals

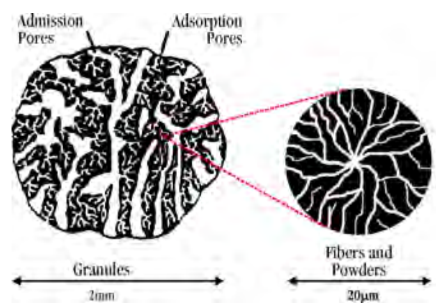


Center for Applied Energy Research

caer.uky.edu

Activated Carbons

- Activated, or porous, carbons are used for a variety of industrial applications
  - including purification of air and water streams;
  - food and pharmaceutical separations; solvent recovery;
  - production of catalysts and catalyst supports..
- Applications (worldwide)
  - Water treatment (40%)
  - air and gas purification (25%)
  - food processing applications (20%).
  - life science applications such as blood dialysis and high purity gases.
  - Emerging applications
  - capacitators and batteries for energy applications
  - hydrogen and nature gas storage

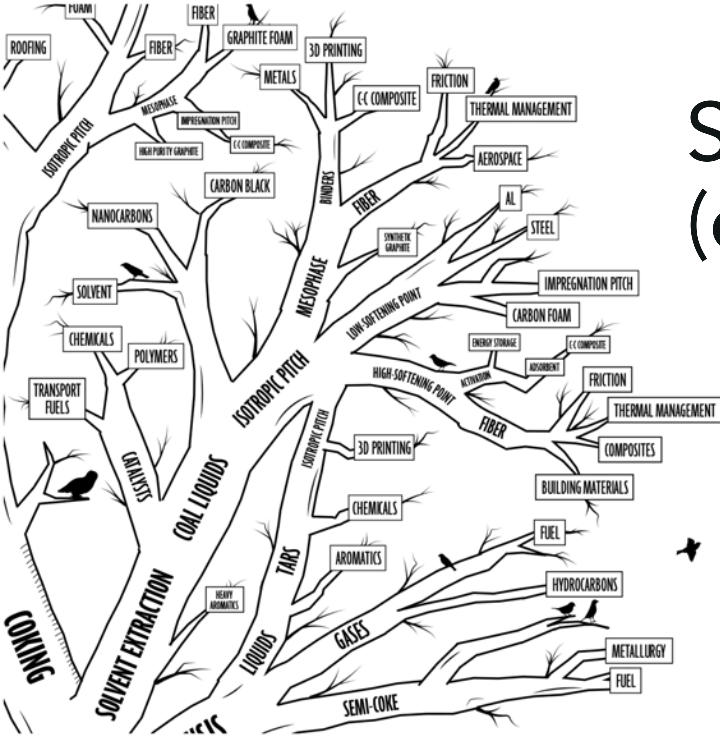


- Production – rotary kiln or multiple hearth furnace
  - coal of various ranks has been traditional starting material
  - physical activation - carbonization (i.e., pyrolysis) followed by partial gasification.
  - chemical activation – use of alkali metal to directly promote gasification
  - flash calcination can be used to produce activated carbon from Powder River Basin coals.
- Carbonization removes non-carbon elements at temperatures of 800-1000^{o}C in the absence of oxygen
- Partial gasification takes in steam, CO_2, air or a combination.
  - Pore structure developed through oxidation and rearrangement of the carbon structure.
- Surface are ranges from 100 – 3,000 m^2/g.

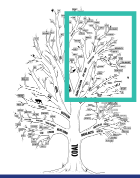
Center for Applied Energy Research

IHS Markit. *Activated Carbon – Chemical Economics Handbook*.
Marsh, H.; Rodriguez-Reinoso, F., *Activated Carbon*. Elsevier: Oxford, UK, 2006.
Wigmans, T., Industrial Aspects of Production and Use of Activated Carbons. *Carbon* 1989, *27* (1), 13-22.

caer.uky.edu



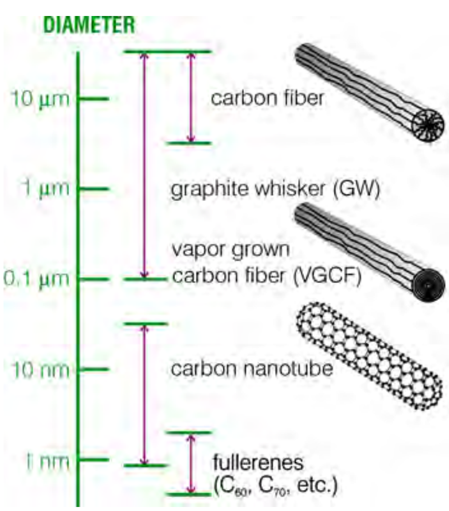
Solvent Extraction (direct liquefaction)

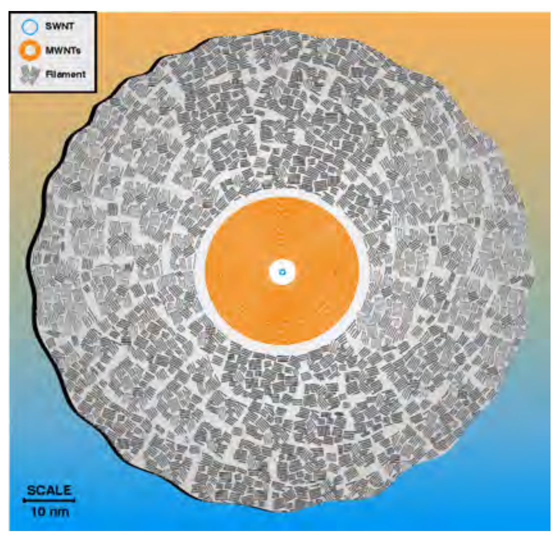


Center for Applied Energy Research

caer.uky.edu

Fibers, nanotubes, and nanofibers





Center for Applied Energy Research

caer.uky.edu

Center for Applied Energy Research

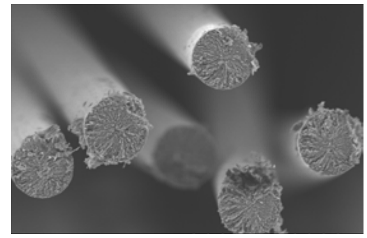
caer.uky.edu

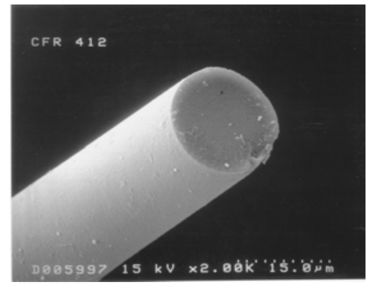
Carbon fiber

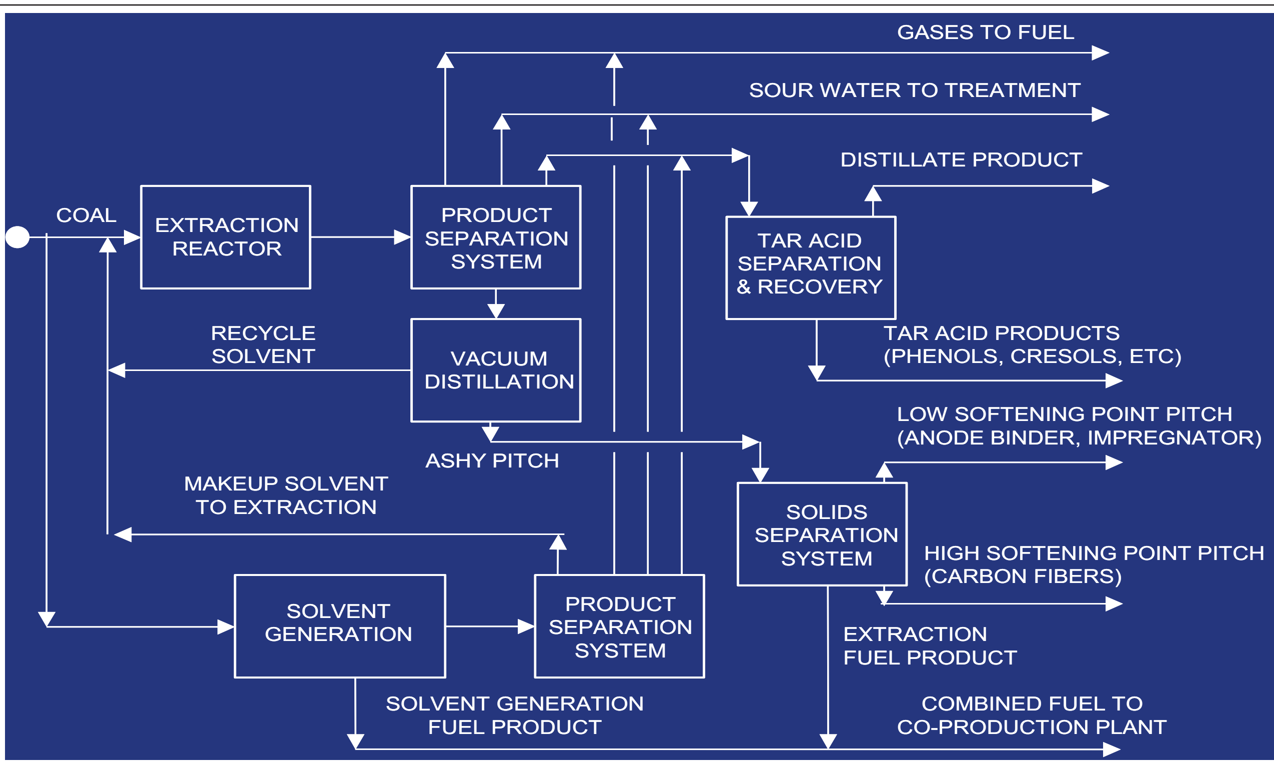
- Mesophase carbon fibers
  - oriented molecular structure
    - liquid crystal phase in pitch
  - high strength, modulus, and thermal conductivity
  - high performance composites, thermal management

- General purpose carbon fibers
  - random molecular orientation in pitch and fiber
  - low modulus, low strength
  - friction, thermal, electrical, filler applications

- Activated carbon fibers
  - from isotropic pitch, PAN, other precursors
  - rapid adsorption kinetics
  - forms (electrically conducting): woven & nonwoven fabrics, paper, felt, rigid monoliths



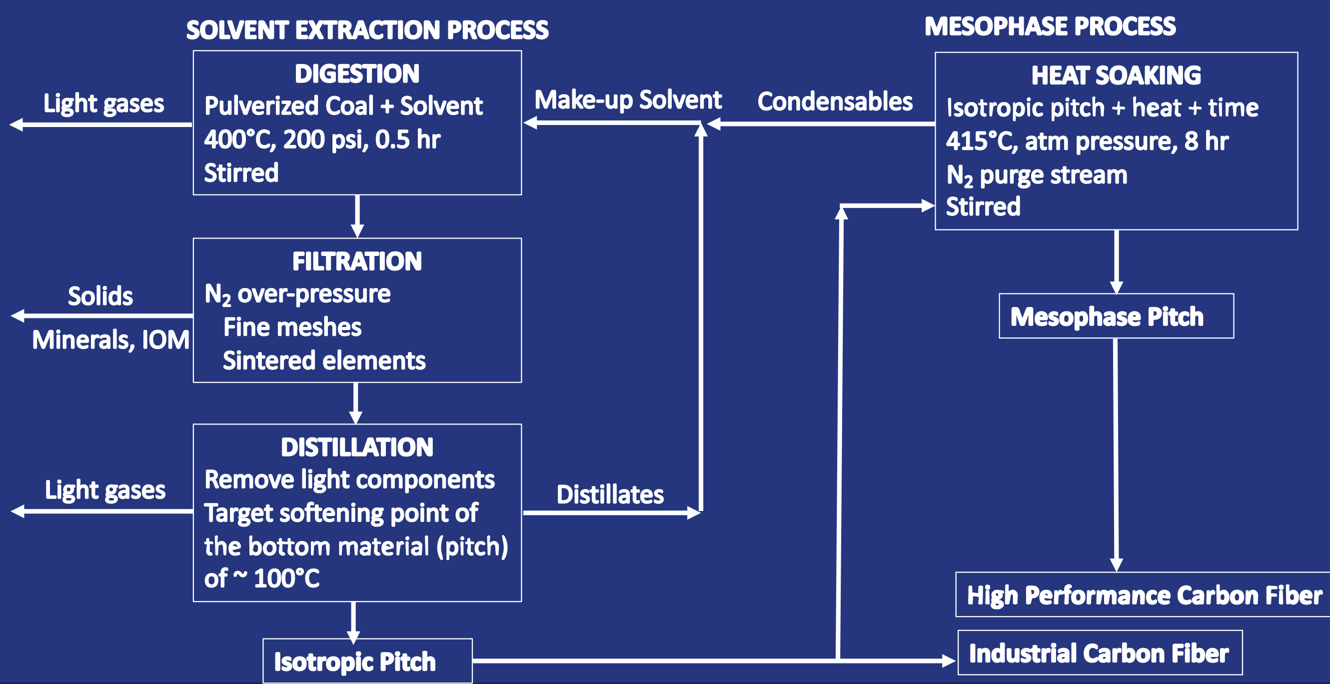




Center for Applied Energy Research

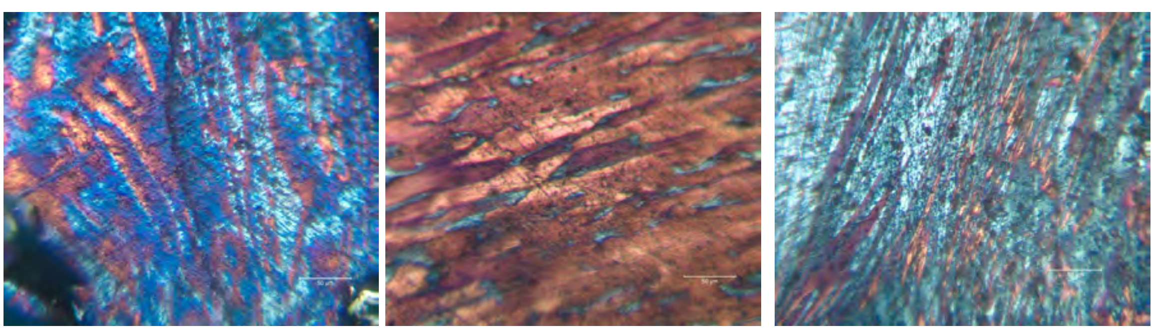
caer.uky.edu

Coal to High Performance Fiber via Mesophase



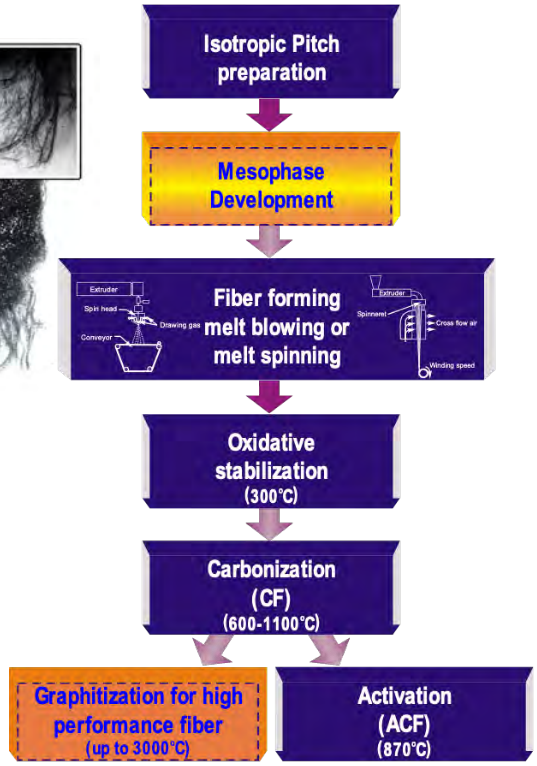
Center for Applied Energy Research caer.uky.edu 15

Mesophase – liquid crystal domain

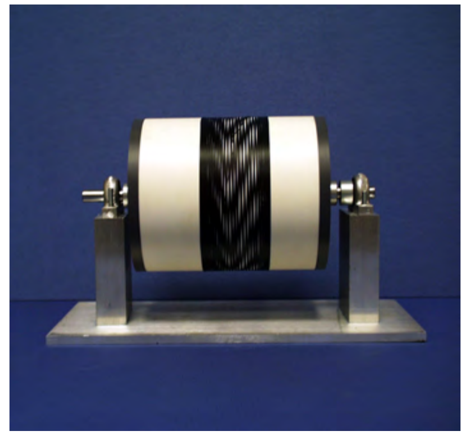


Reflected light, polarized optical micrographs of spinnable coal tar mesophase pitches. Achieved 100% mesophase in the range of 305°C softening point.

Center for Applied Energy Research caer.uky.edu



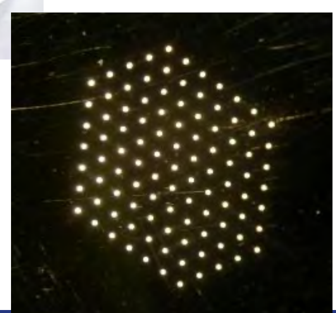
Stages of carbon fiber synthesis



caer.uky.edu

Challenges with carbon fiber from coal

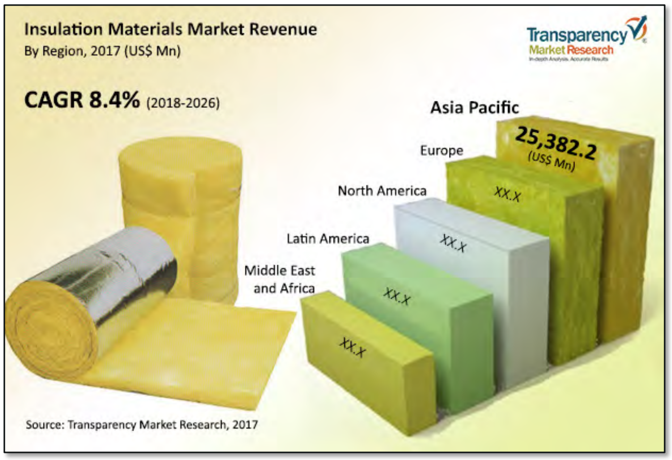
- Ash – plug spinnerets, stops mesophase coalescences, results in rough fiber surfaces, and acts as point failure defect
- Sulfur – puffs during oxidation
- Too low or too high softening point
- Cost of producing synthetic pitch
- Cost of thermal treatments
- Ash
- Ash
- Ash



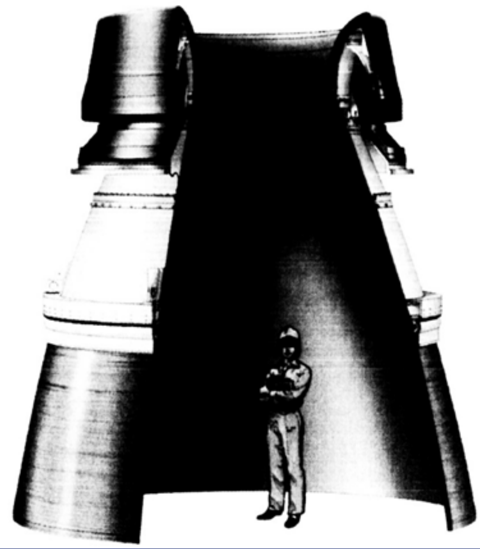
Center for Applied Energy Research

caer.uky.edu

Low thermal conductivity carbon fibers could be used for building thermal insulation



There is a need to replace rayon-derived carbon fibers for aerospace applications



Kenneth P. Wilson (2002)
ATK/Thiokol Propulsion R&D Laboratories

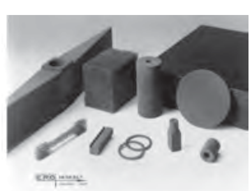
Center for Applied Energy Research | caer.uky.edu

Carbon Materials Applications

Graphite
Nuclear Reactors
Metals Processing
High Temperature Components
Sliding Contacts (e.g. Trains)
Electric Motor Brushes
Heat Management / Cooling
Lubricants

Carbon Fibers & Composites
Airplanes / Rockets / Spacecraft
Sports Equipment
Defense – Armor / Structures
Automotive Components
Bridge and Building Repair
Aircraft and Automotive Brakes

Industrial Pitch & Coke
Arc Furnaces (Steel Making)
Aluminum Production
High Temperature Vessels
Glass Processing
Seals and Gaskets
Roofing and Construction
Rubber
Wood Preservatives



Carbon Black
Tires
Plastics
Electronics Packaging
Chemical Production
Paints and Coatings
Batteries

Activated Carbons
Water & Air Purification
Industrial Separations
Gas Processing
Food and Beverage
Medical/Pharmaceutical
Chem/Bio Defense
Batteries and Capacitors

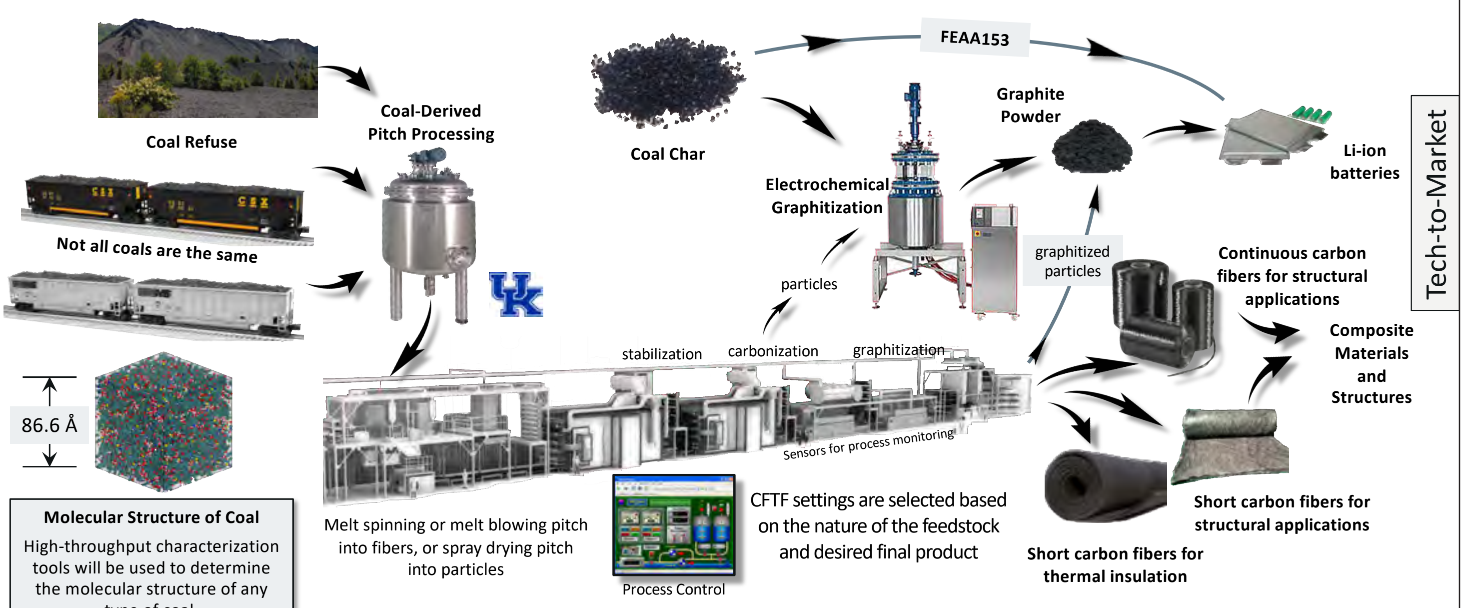
Center for Applied Energy Research | caer.uky.edu

ORNL's Carbon Fiber Technology Facility (CFTF)

Established in 2013, the CFTF is the Department of Energy's only designated user facility for carbon fiber innovation.

- 42,000 sq. ft. facility
- 390 ft. long processing line, capable of custom unit operation configuration
- Up to 25 tons per year

Carbon Ore and Coal Refuse-to-Products at ORNL's Carbon Fiber Technology Facility



Molecular Structure of Coal

High-throughput characterization tools will be used to determine the molecular structure of any type of coal.

Center for Applied Energy Research

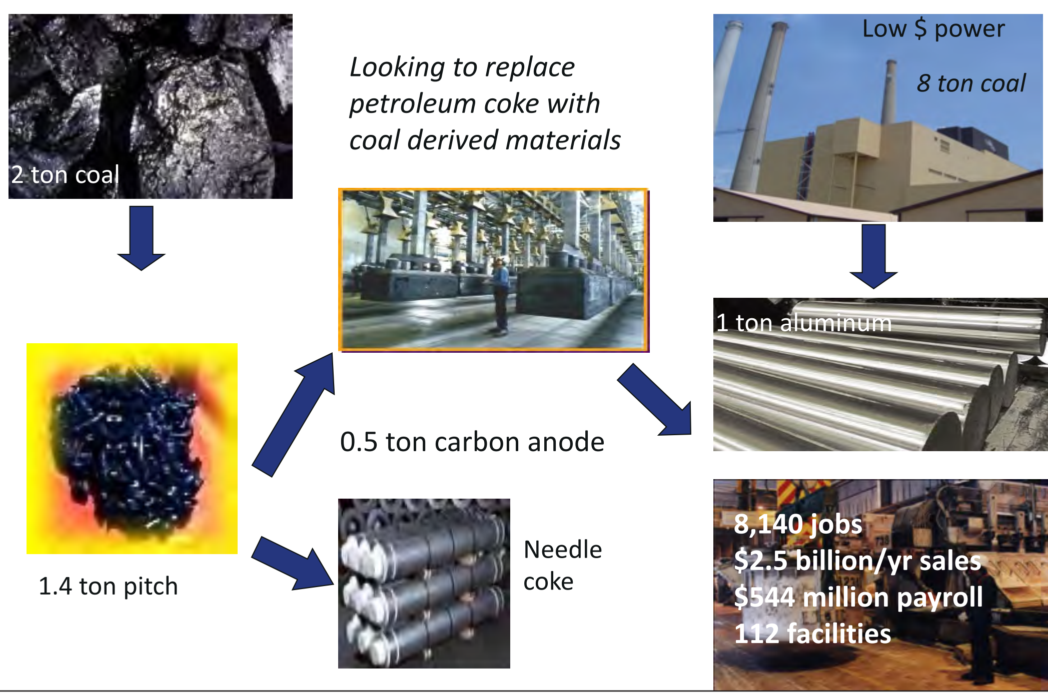
caer.uky.edu

Nanotubes and nanofibers

- Both nanotubes and nanofibers have been produced from coal liquids or aromatic feedstocks
- Nanotubes
  - Generally require neat solvent with high purity
  - To date, coal derived CNT's have been multiwalled
- Nanofibers
  - Early work by Applied Sciences Inc (subsequently at WVU)
  - Can be more tolerant of impurities, and often benefit from S
- Commercially still a curiosity due to costs

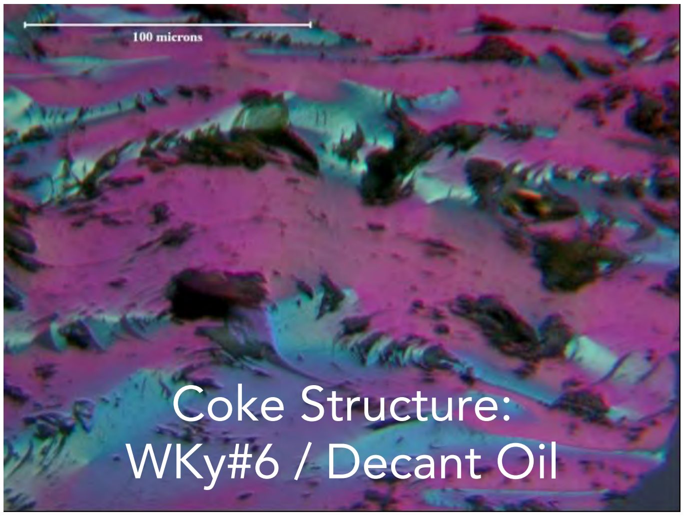
Center for Applied Energy Research caer.uky.edu

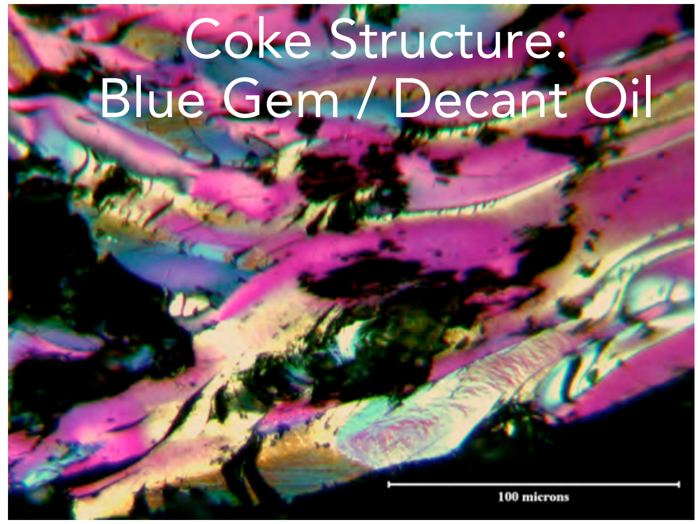
Carbon Materials, Aluminum and Kentucky



Center for Applied Energy Research caer.uky.edu

Needle coke from coal extracts





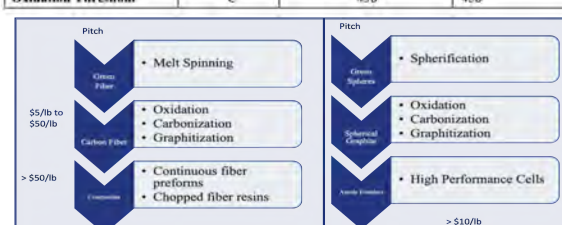
Center for Applied Energy Research

caer.uky.edu

Synthetic Graphite

Table 4. Coal-Derived Graphite Property Targest

GRAPHITE			
	Units	Commercial Synthetic Isomolded Graphite	Coal Derived Graphite (target)
Target Graphite Grade		Poco EDM-3	Isomolded
Flake (Particle) Size	Micron	<5	<5
Flake (Particle) Thickness	Micron	n/a	n/a
% Carbon	%	99.8	> 99.8
% Ash	%	0.2	< 0.2
Porosity	%	20	< 20
Surface Area	m^2/g	n/a	n/a
Bulk Density	g/cm^3	1.78	> 1.75
Hardness	Shore	73	> 70
Extent of Graphitization	%	n/a	n/a
Specific Resistance	Ohm.cm	0.00156	< 0.0017
Modulus of Elasticity	MPa	11,000	> 10,000
Flexural Strength	MPa	92	> 85
Tensile Strength	MPa	62	> 60
Compressive Strength	MPa	138	> 120
Specific Heat	J/(g.K)	0.72	0.72
Coefficient of Thermal Expansion	10^{-6} (cm/cm/K)	7.9	< 8
Thermal Conductivity	W/K.m	95	> 90
Thermal Shock Resistance	W/m	n/a	n/a
Oxidation Threshold	°C	450	450

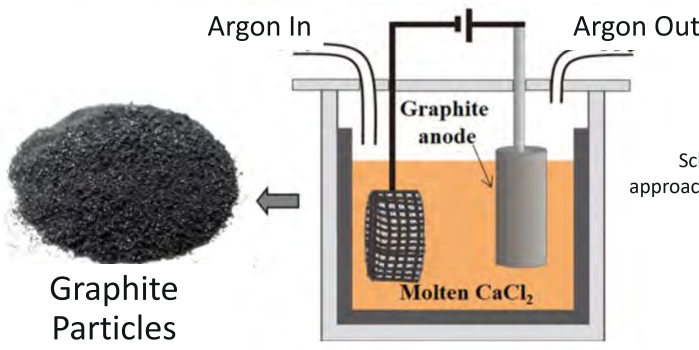


Center for Applied Energy Research

caer.uky.edu

Scale up process for electrochemical graphitization of carbon particles

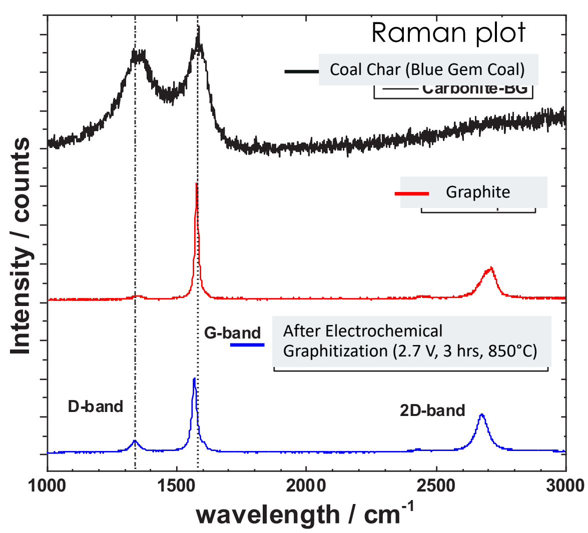
Cathodic polarization of amorphous carbon in molten $MgCl_2$ at ~850°C leads to its transformation into graphite.



Schematic of electrochemical approach for the synthesis of graphite.[1,2]

1. Angewandte Chemie, **2017**, *129(7)*, 1777-1781.
2. Chemistry–A European Journal, **2017**, *23(48)*, 11455-11459.

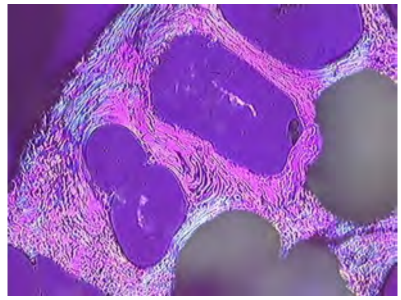
Electrochemically Graphitization of Coal Char



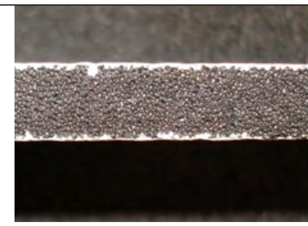
- Raman spectroscopy data confirmed successful graphitization.
  - Low I_D/I_G ratio on Raman

Carbon Foam Applications

- Lightweight, high rigidity
- Thermal management
  - Low conductivity insulation
  - Highly graphitic conductor
- Electromagnetic Shielding
  - With or without other additives
  - Fe_3O4 and ZnO nanoparticles
- Blast mitigation
- Building materials



Andrews and Zondlo



Ceramic slip encapsulated graphite foam shingles. UK CAER.

Center for Applied Energy Research

caer.uky.edu

Carbon Dots

Fuel

Full Length Article

Functional carbon dots from a mild oxidation of coal liquefaction residue

Fuwei Qin, Qiqi Li, Tingting Tang, Jiayao Zhu, Xuemeng Gan, Yaoyao Chen, Yizhao Li, Su Zhang, Xueli Huang, Dianzeng Jia

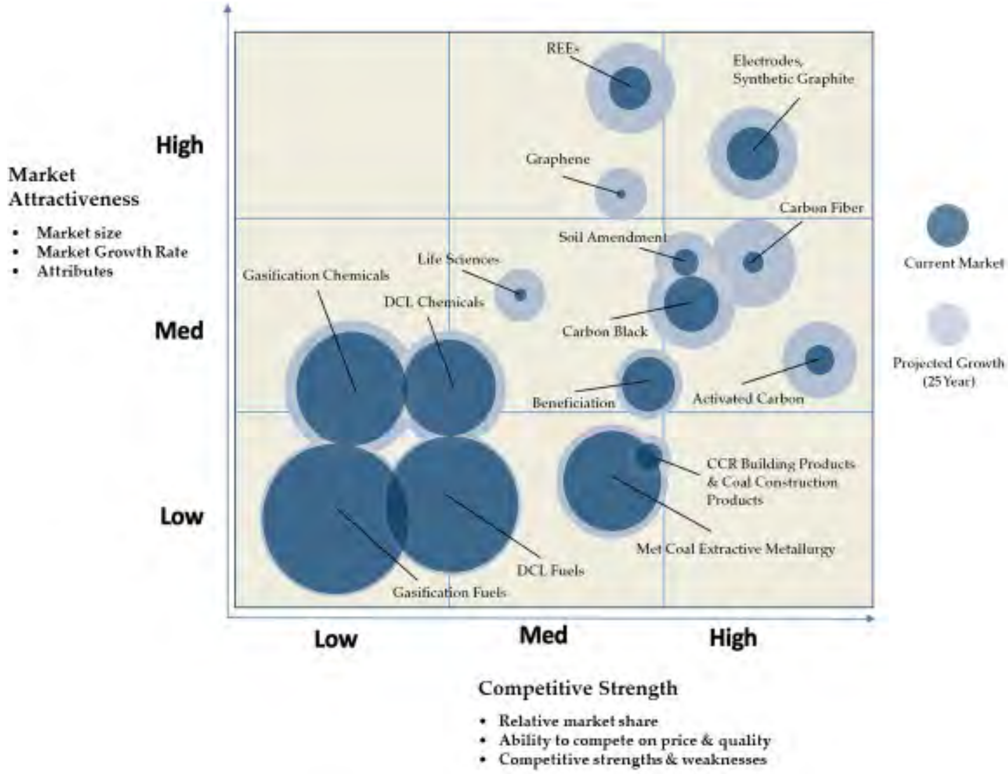
Center for Applied Energy Research

caer.uky.edu

Center for Applied Energy Research

caer.uky.edu

The value of carbon materials



Source: National Coal Council, "Coal in a New Carbon Age"

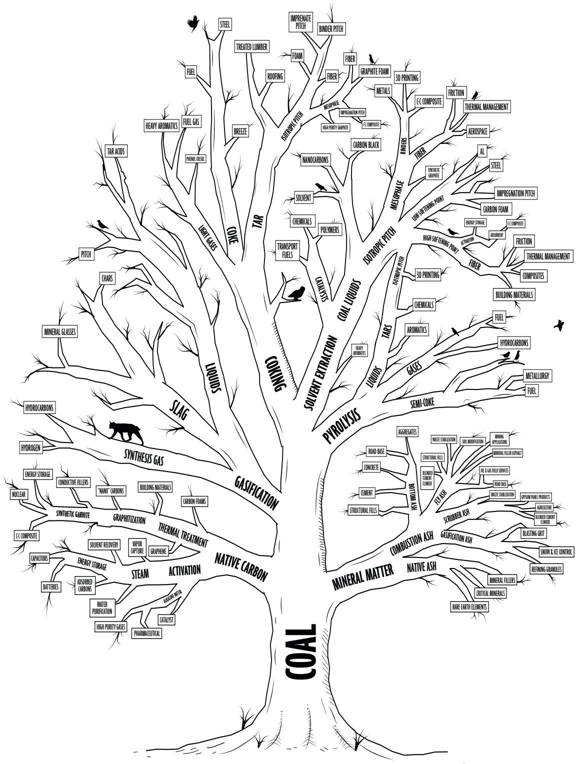
New opportunities

- Energy Storage
  - porous carbons
  - conductivity modifiers
  - conductive plates
- Building materials
  - Durable outdoor materials
  - Energy efficiency
- Organic electronics and 3D printable materials
- Rare earth elements and critical minerals
  - not actually carbon materials, other than graphite

Center for Applied Energy Research caer.uky.edu

Center for Applied Energy Research

Questions?



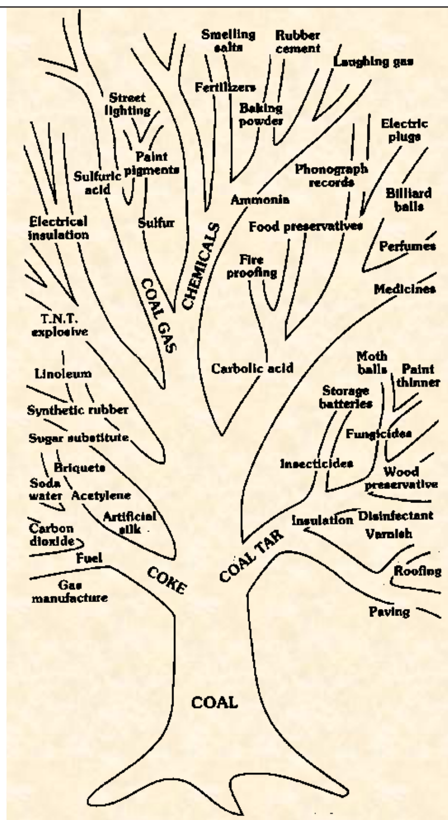
Rodney Andrews, PhD PE
Center for Applied Energy Research
University of Kentucky
rodney.andrews@uky.edu

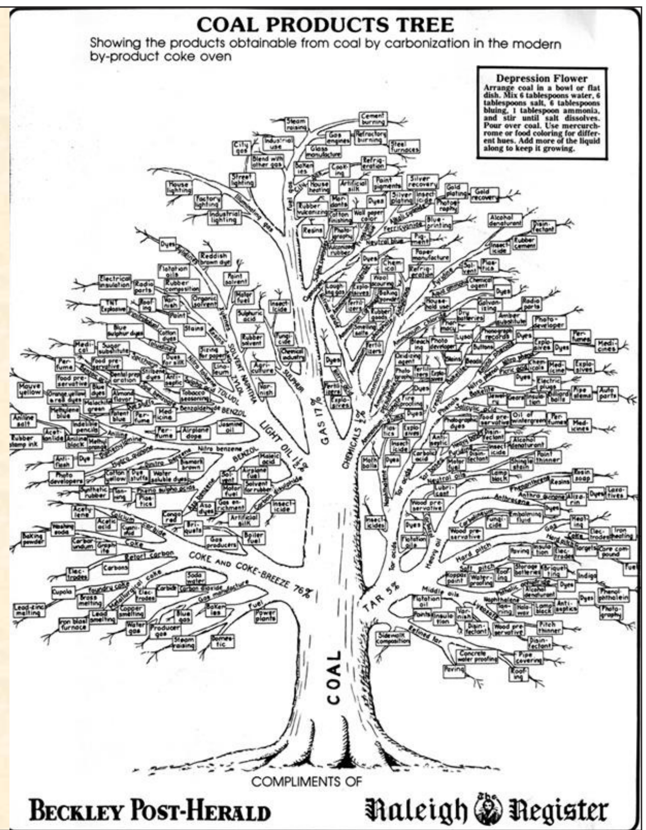
caer.uky.edu

Center for Applied Energy Research

"Revisit the Coal Tree in light of emerging technologies in carbon materials and coal-derived value-added products."

-Me. 2001.





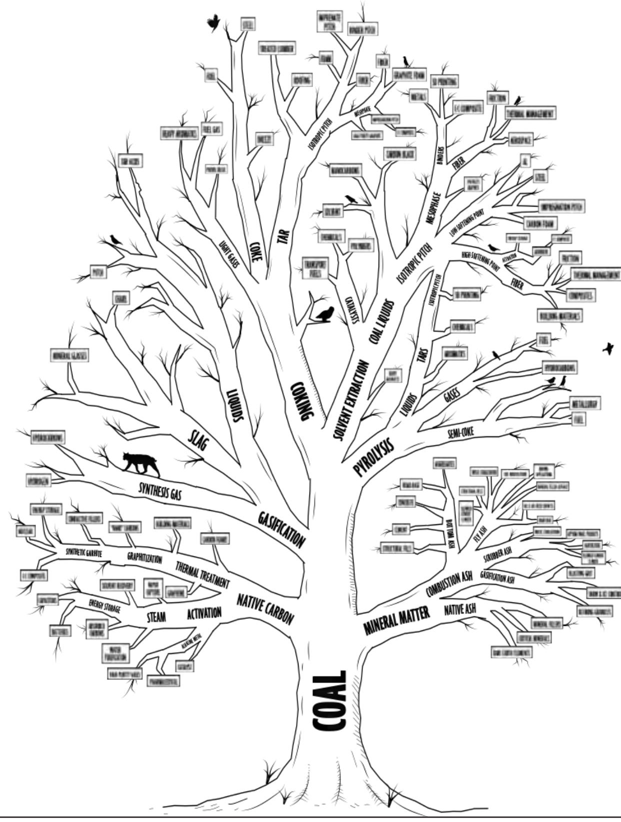
caer.uky.edu

Center for Applied Energy Research

caer.uky.edu

A New Coal Tree:

Materials science advances and modern societal demand have fundamentally changed what opportunities coal offers in developing new economic activity and job creation in the nation's coal basins.

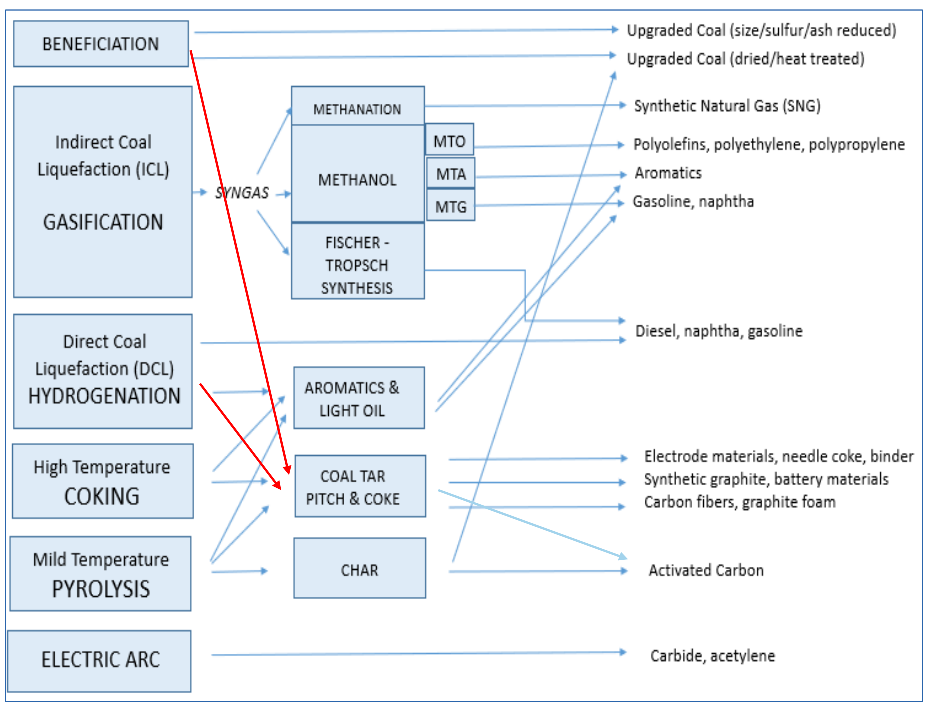


Andrews, Weisenberger, Jewell and Puckett. 2022.

Center for Applied Energy Research

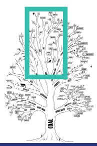
caer.uky.edu

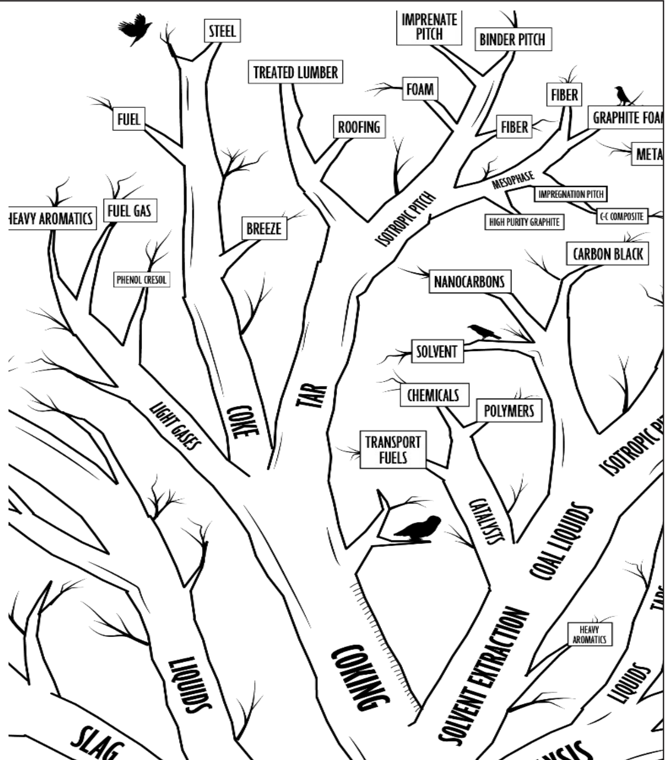
Production Pathways



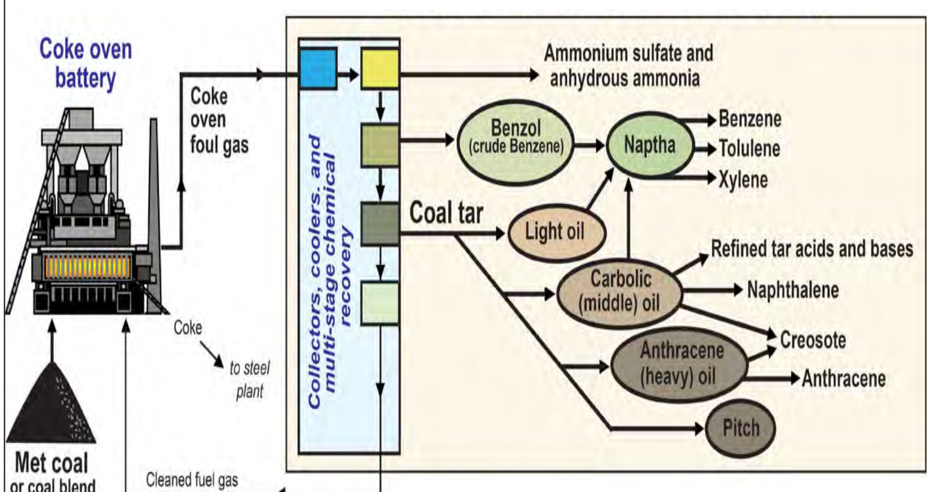
Coal Coking

- Produce metallurgical coke
- Partial combustion of coal and recycle fuel gas
- High temperature – low oxygen
  - gases
  - condensables
  - tars and tar acids
- Traditional source of binder pitch





Coke byproduct recovery

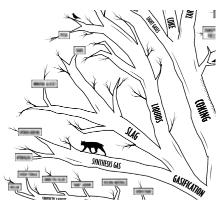


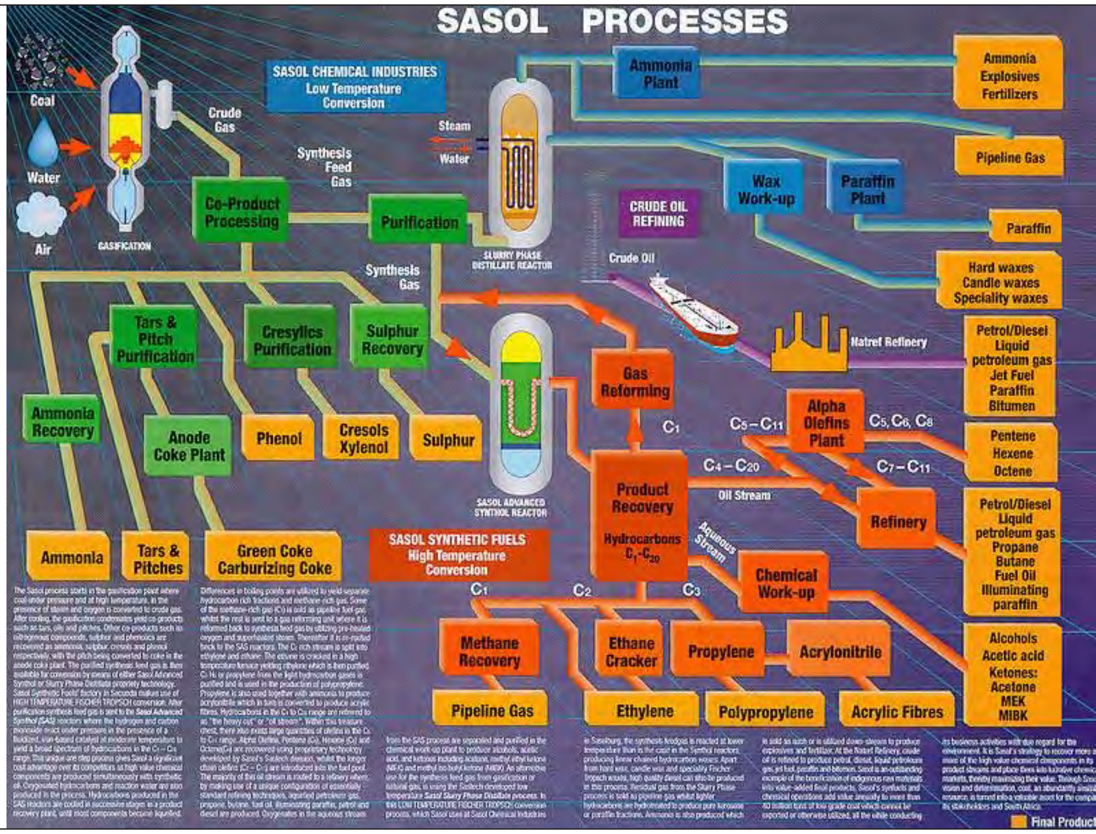
- Binder pitch
- Roofing pitch
- Road Tar
- Friction materials
- Steel
- Aluminum

Kentucky Geological Survey
US Steel

Center for Applied Energy Research

Gasification Products





caer.uky.edu

INDIANA GEOLOGICAL
& WATER SURVEY
INDIANA UNIVERSITY

ORGANIC-MATTER-RICH PENNSYLVANIAN BLACK SHALES AS A SOURCE OF CRITICAL MINERALS

Maria Mastalerz, Agnieszka Drobniak, and Philip Ames

Indiana Geological and Water Survey, Indiana University, 1001 E. 10th St., Bloomington, IN 47405, USA

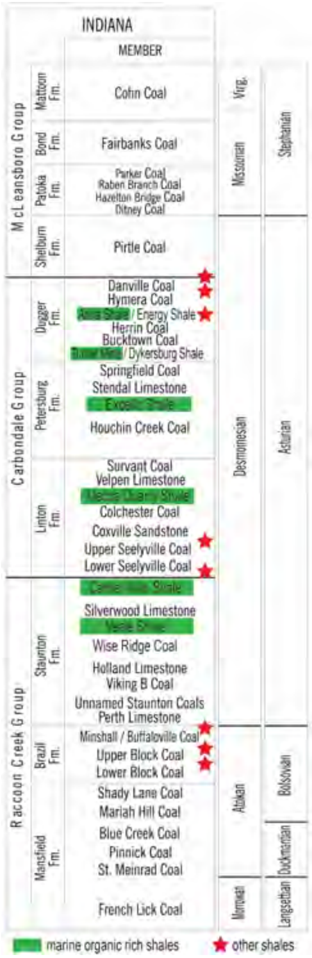
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

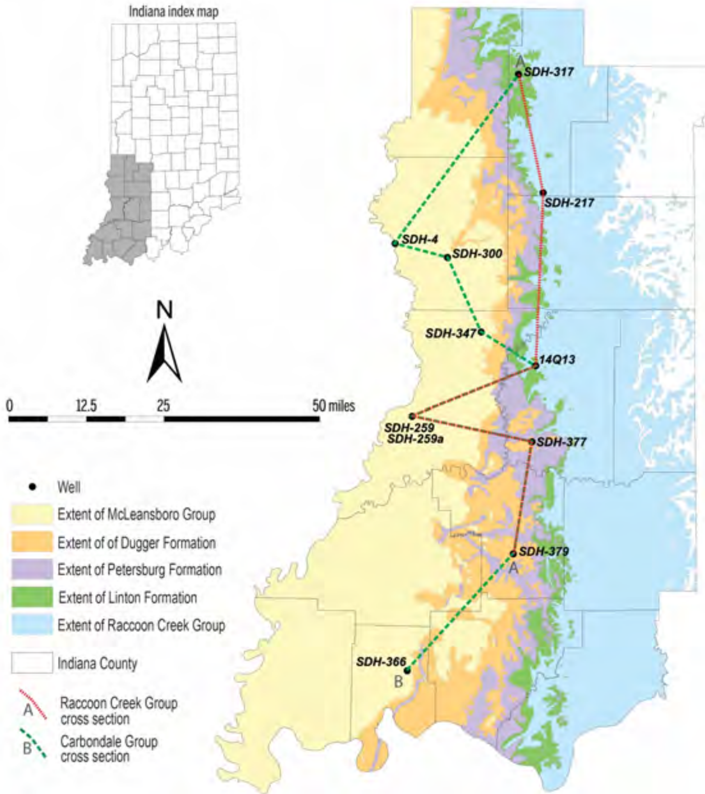
SOME FACTS ABOUT PENNSYLVANIAN BLACK SHALES

- Organic-matter-rich black shales of midcontinent North America are part of Pennsylvanian cyclothems (repeated sequences of transgressive marine limestone, marine black shales, regressive marine limestone, nearshore to terrestrial shale, and paleosols and coals)
- Within the cyclothems, marine black shales represent the maximum flooding surface and the high stand of sea level
- Rich in organic matter; TOC typically ranges from 4 to 40 %. They also produce a high response on gamma-ray logs
- Black shales have long been known to be enriched in various metals, such as Zn, Mo, or U
- Many studies suggest that the mineralization took place during sedimentation and early diagenesis by direct precipitation of sulfide minerals or by interaction between metals dissolved in the sea water and organic matter although others suggested the possibility of additional diagenetic enrichment from metal-rich fluids
- With the recent interest in critical minerals, the purpose of this study is to expand a geochemical database of Pennsylvanian black shales and to get a better understanding of their potential as a source of selected elements, especially for REE, V, Zn, and As.

INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

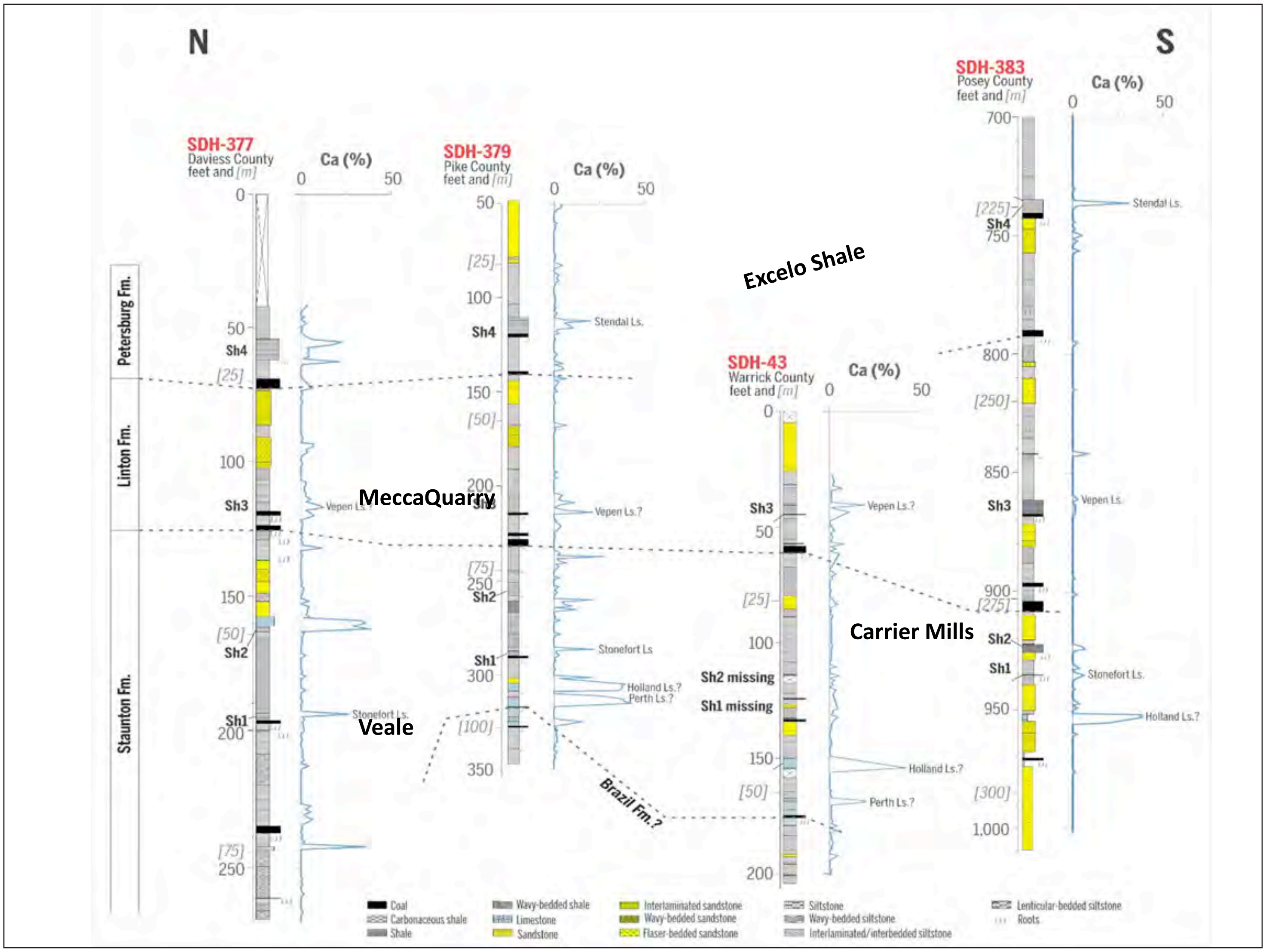
METHODOLOGY



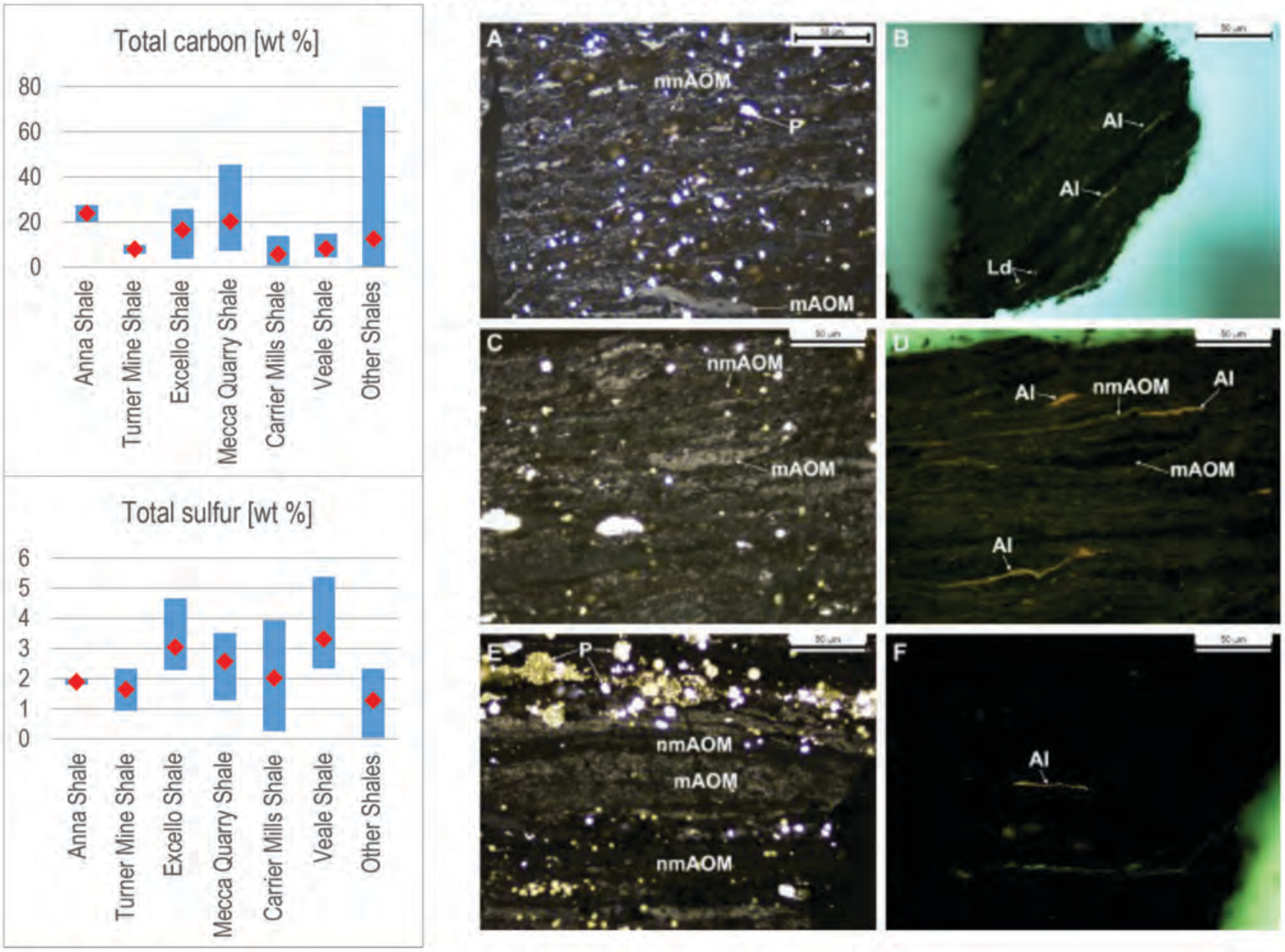


From Mastalerz et al., 2022

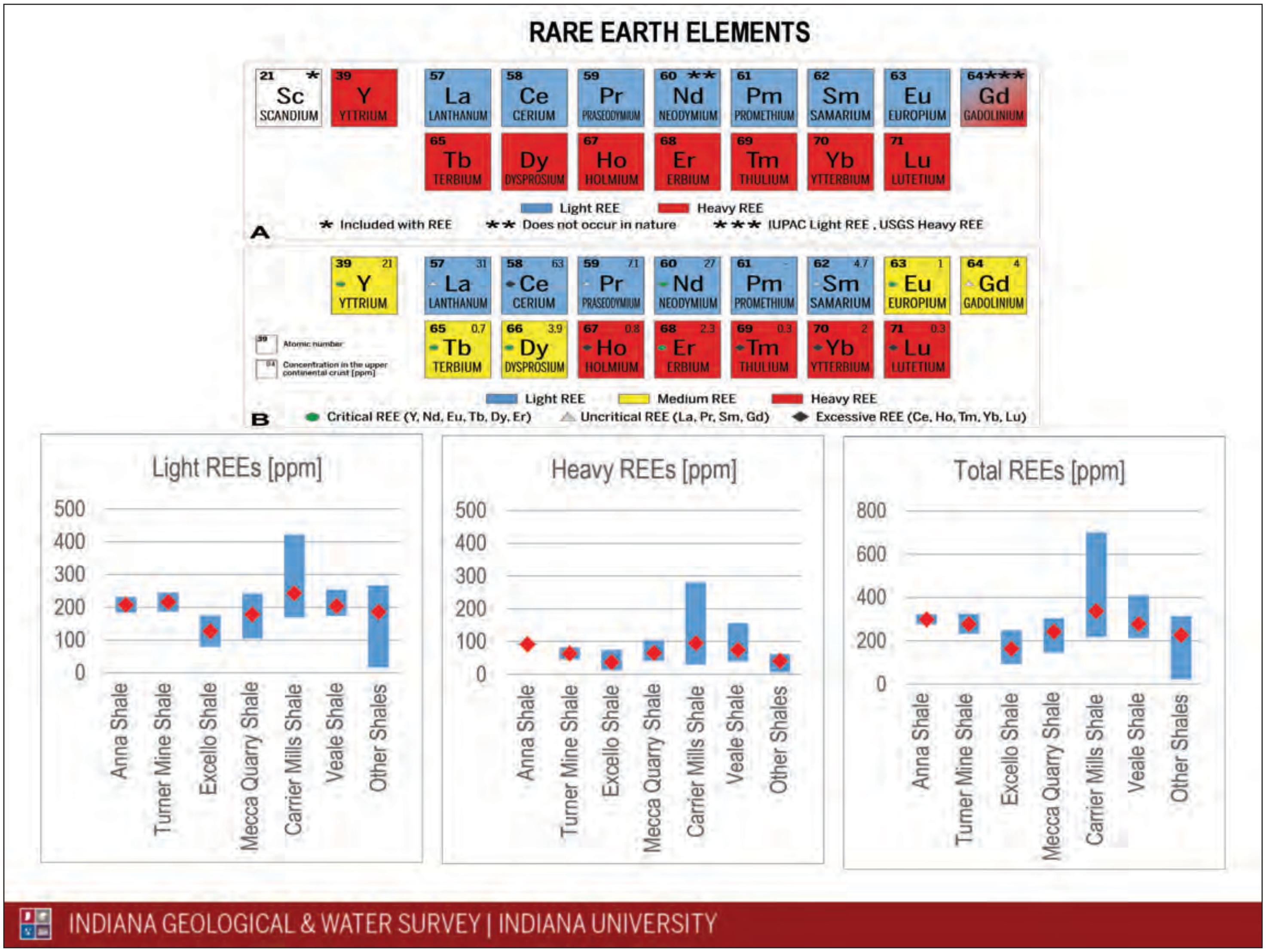
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

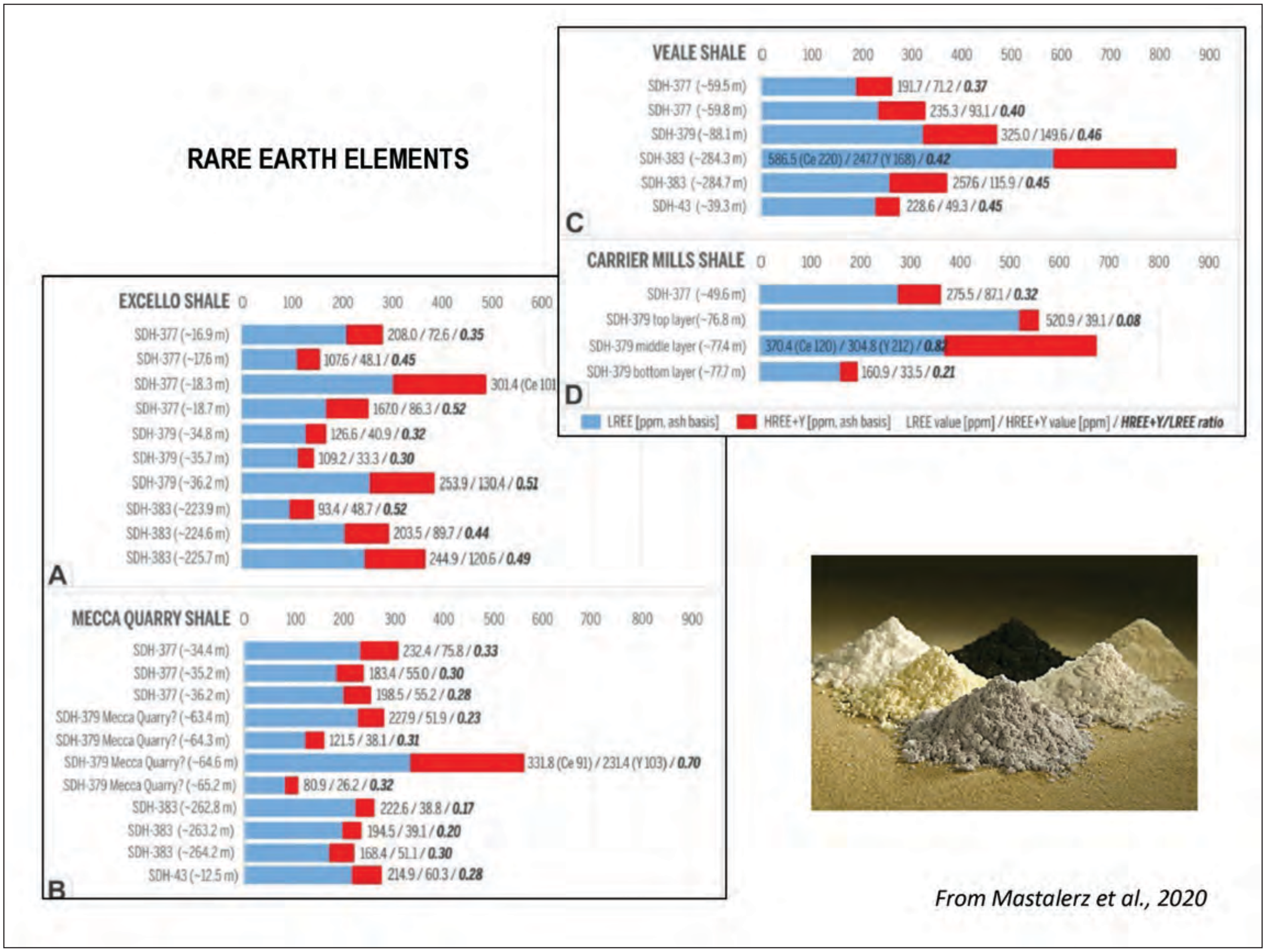

N
S
SDH-377
Daviess County
feet and [m]
Ca (%)
SDH-379
Pike County
feet and [m]
SDH-43
Warrick County
feet and [m]
SDH-383
Posey County
feet and [m]
Petersburg Fm.
Linton Fm.
Staunton Fm.
Excelo Shale
MeccaQuarry
Veale
Carrier Mills
Brazil Fm.?
Sh1
Sh2
Sh3
Sh4
Sh2 missing
Sh1 missing
Stendal Ls.
Vepen Ls.?
Vepen Ls.
Stonefort Ls.
Holland Ls.?
Perth Ls.?
Coal
Carbonaceous shale
Shale
Wavy-bedded shale
Limestone
Sandstone
Interlaminated sandstone
Wavy-bedded sandstone
Flaser-bedded sandstone
Siltstone
Wavy-bedded siltstone
Interlaminated/interbedded siltstone
Lenticular-bedded siltstone
Roots

CARBON and SULFUR CONTENT



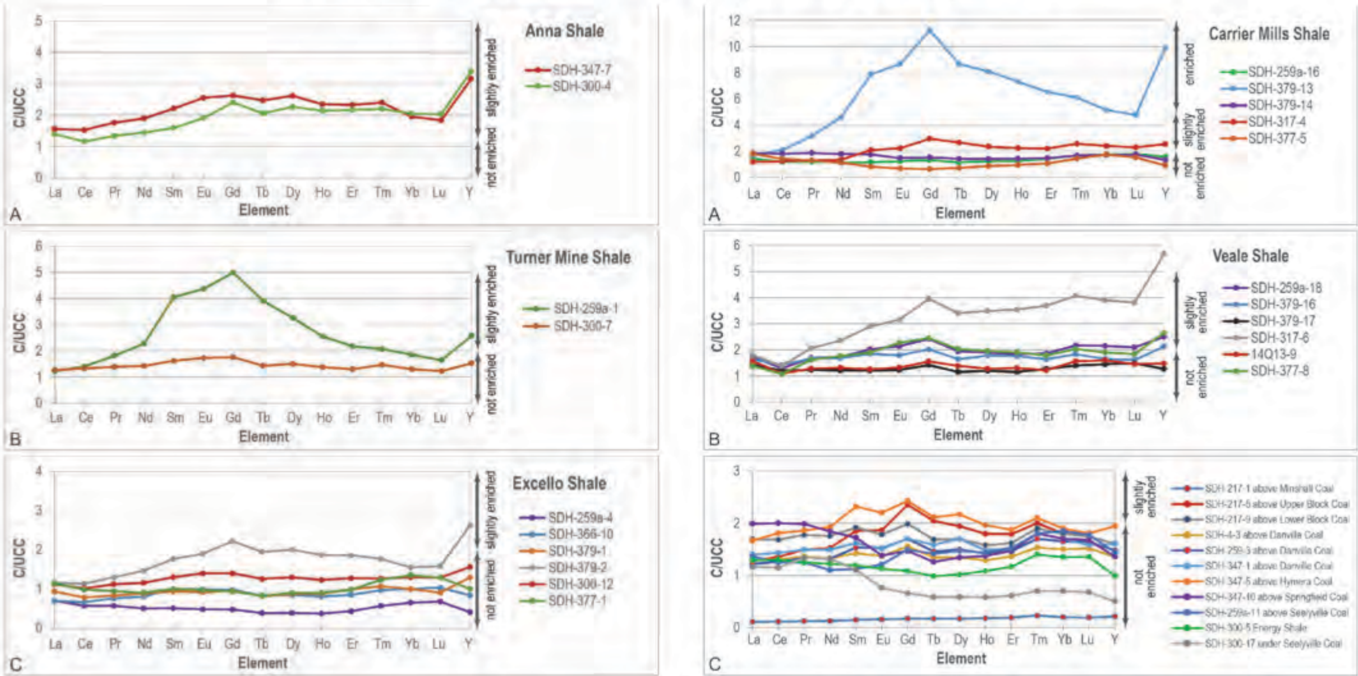
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

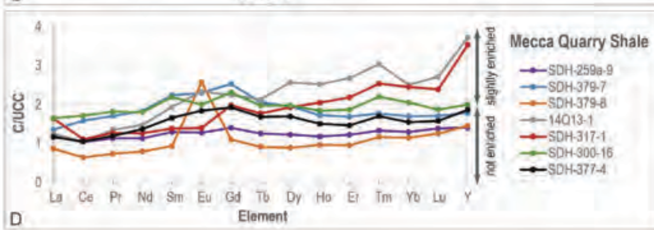

RARE EARTH ELEMENTS
21 * Sc SCANDIUM
39 Y YTTRIUM
57 La LANTHANUM
58 Ce CERIUM
59 Pr PRASEODYMIUM
60 ** Nd NEODYMIUM
61 Pm PROMETHIUM
62 Sm SAMARIUM
63 Eu EUROPIUM
64*** Gd GADOLINIUM
65 Tb TERBIUM
Dy DYSPROSIUM
67 Ho HOLMIUM
68 Er ERBIUM
69 Tm THULIUM
70 Yb YTTERBIUM
71 Lu LUTETIUM
Light REE
Heavy REE
A
* Included with REE
** Does not occur in nature
*** IUPAC Light REE , USGS Heavy REE
39 21 Y YTTRIUM
57 31 La LANTHANUM
58 63 Ce CERIUM
59 7.1 Pr PRASEODYMIUM
60 27 Nd NEODYMIUM
61 Pm PROMETHIUM
62 4.7 Sm SAMARIUM
63 1 Eu EUROPIUM
64 4 Gd GADOLINIUM
65 0.7 Tb TERBIUM
66 3.9 Dy DYSPROSIUM
67 0.8 Ho HOLMIUM
68 2.3 Er ERBIUM
69 0.3 Tm THULIUM
70 2 Yb YTTERBIUM
71 0.3 Lu LUTETIUM
Atomic number
Concentration in the upper continental crust [ppm]
Light REE
Medium REE
Heavy REE
B
Critical REE (Y, Nd, Eu, Tb, Dy, Er)
Uncritical REE (La, Pr, Sm, Gd)
Excessive REE (Ce, Ho, Tm, Yb, Lu)
Light REEs [ppm]
500
400
300
200
100
0
Anna Shale
Turner Mine Shale
Excello Shale
Mecca Quarry Shale
Carrier Mills Shale
Veale Shale
Other Shales
Heavy REEs [ppm]
500
400
300
200
100
0
Anna Shale
Turner Mine Shale
Excello Shale
Mecca Quarry Shale
Carrier Mills Shale
Veale Shale
Other Shales
Total REEs [ppm]
800
600
400
200
0
Anna Shale
Turner Mine Shale
Excello Shale
Mecca Quarry Shale
Carrier Mills Shale
Veale Shale
Other Shales
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY



RARE EARTH ELEMENTS
VEALE SHALE 0 100 200 300 400 500 600 700 800 900
SDH-377 (~59.5 m) 191.7 / 71.2 / 0.37
SDH-377 (~59.8 m) 235.3 / 93.1 / 0.40
SDH-379 (~88.1 m) 325.0 / 149.6 / 0.46
SDH-383 (~284.3 m) 586.5 (Ce 220) / 247.7 (Y 168) / 0.42
SDH-383 (~284.7 m) 257.6 / 115.9 / 0.45
SDH-43 (~39.3 m) 228.6 / 49.3 / 0.45
C
CARRIER MILLS SHALE 0 100 200 300 400 500 600 700 800 900
SDH-377 (~49.6 m) 275.5 / 87.1 / 0.32
SDH-379 top layer(~76.8 m) 520.9 / 39.1 / 0.08
SDH-379 middle layer (~77.4 m) 370.4 (Ce 120) / 304.8 (Y 212) / 0.82
SDH-379 bottom layer (~77.7 m) 160.9 / 33.5 / 0.21
D
LREE [ppm, ash basis] HREE+Y [ppm, ash basis] LREE value [ppm] / HREE+Y value [ppm] / HREE+Y/LREE ratio
EXCELLO SHALE 0 100 200 300 400 500 600
SDH-377 (~16.9 m) 208.0 / 72.6 / 0.35
SDH-377 (~17.6 m) 107.6 / 48.1 / 0.45
SDH-377 (~18.3 m) 301.4 (Ce 101
SDH-377 (~18.7 m) 167.0 / 86.3 / 0.52
SDH-379 (~34.8 m) 126.6 / 40.9 / 0.32
SDH-379 (~35.7 m) 109.2 / 33.3 / 0.30
SDH-379 (~36.2 m) 253.9 / 130.4 / 0.51
SDH-383 (~223.9 m) 93.4 / 48.7 / 0.52
SDH-383 (~224.6 m) 203.5 / 89.7 / 0.44
SDH-383 (~225.7 m) 244.9 / 120.6 / 0.49
A
MECCA QUARRY SHALE 0 100 200 300 400 500 600 700 800 900
SDH-377 (~34.4 m) 232.4 / 75.8 / 0.33
SDH-377 (~35.2 m) 183.4 / 55.0 / 0.30
SDH-377 (~36.2 m) 198.5 / 55.2 / 0.28
SDH-379 Mecca Quarry? (~63.4 m) 227.9 / 51.9 / 0.23
SDH-379 Mecca Quarry? (~64.3 m) 121.5 / 38.1 / 0.31
SDH-379 Mecca Quarry? (~64.6 m) 331.8 (Ce 91) / 231.4 (Y 103) / 0.70
SDH-379 Mecca Quarry? (~65.2 m) 80.9 / 26.2 / 0.32
SDH-383 (~262.8 m) 222.6 / 38.8 / 0.17
SDH-383 (~263.2 m) 194.5 / 39.1 / 0.20
SDH-383 (~264.2 m) 168.4 / 51.1 / 0.30
SDH-43 (~12.5 m) 214.9 / 60.3 / 0.28
B
From Mastalerz et al., 2020

PATTERNS of RARE EARTH ELEMENTS of BLACK SHALES





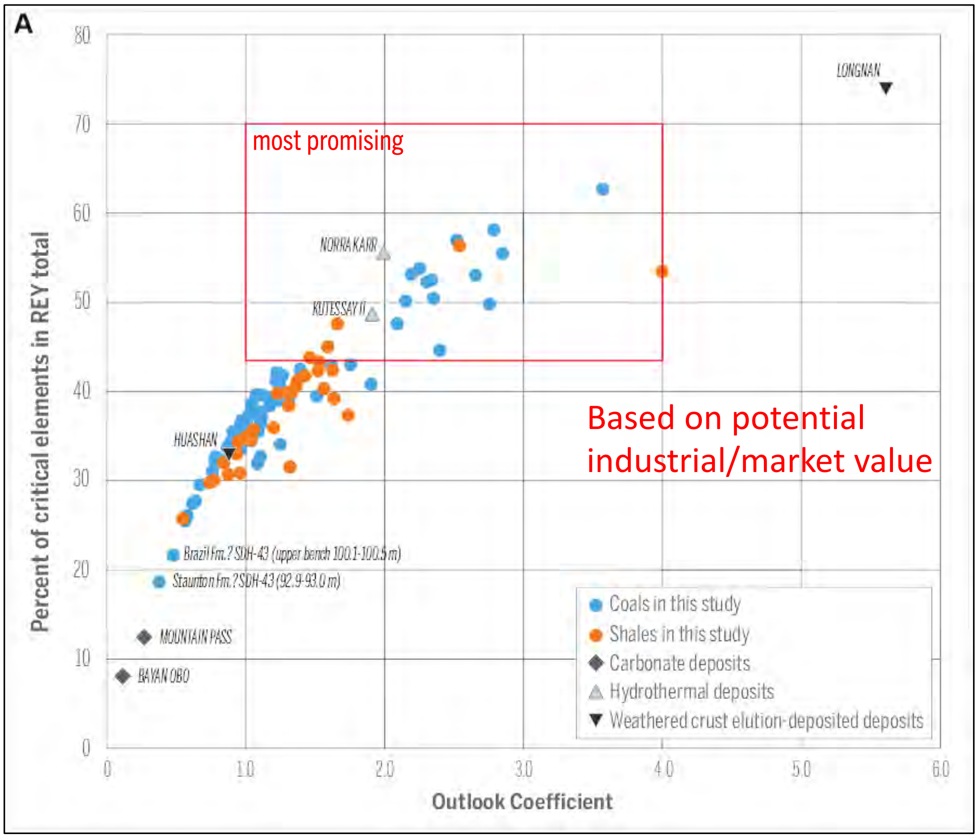
Some samples show very little fractionation, but some show positive anomalies for Gd and one sample of the Mecca Quarry Shale has a positive Eu anomaly. The REE distribution patterns show that the majority of shales have REE values that are roughly representative of the upper continental crust (UCC). Some samples are slightly enriched in some elements (C/UCC values of 2 to 5) and only one sample of the Carrier Mills Shale is considered enriched

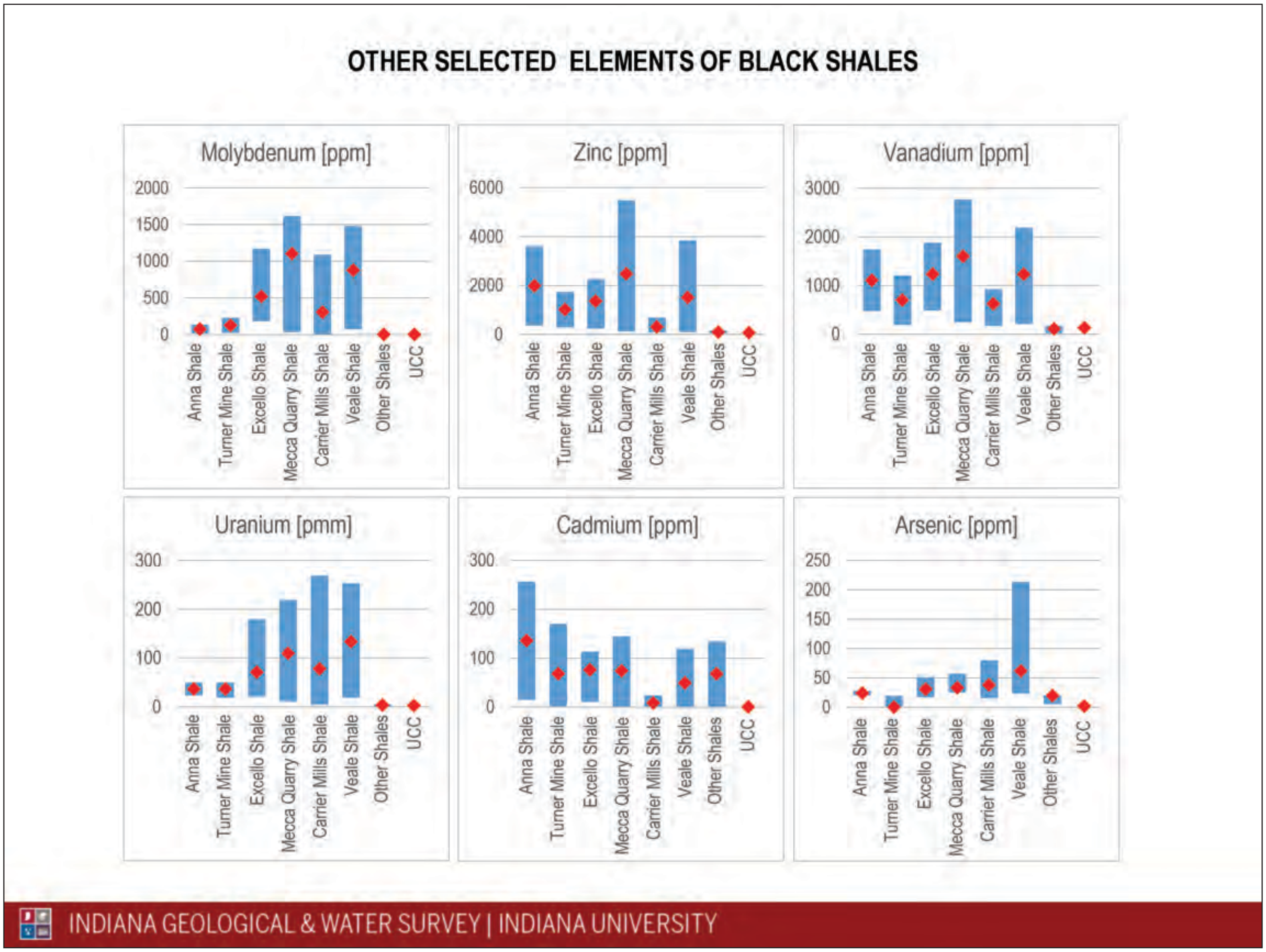
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

How can we evaluate REE resource quality?

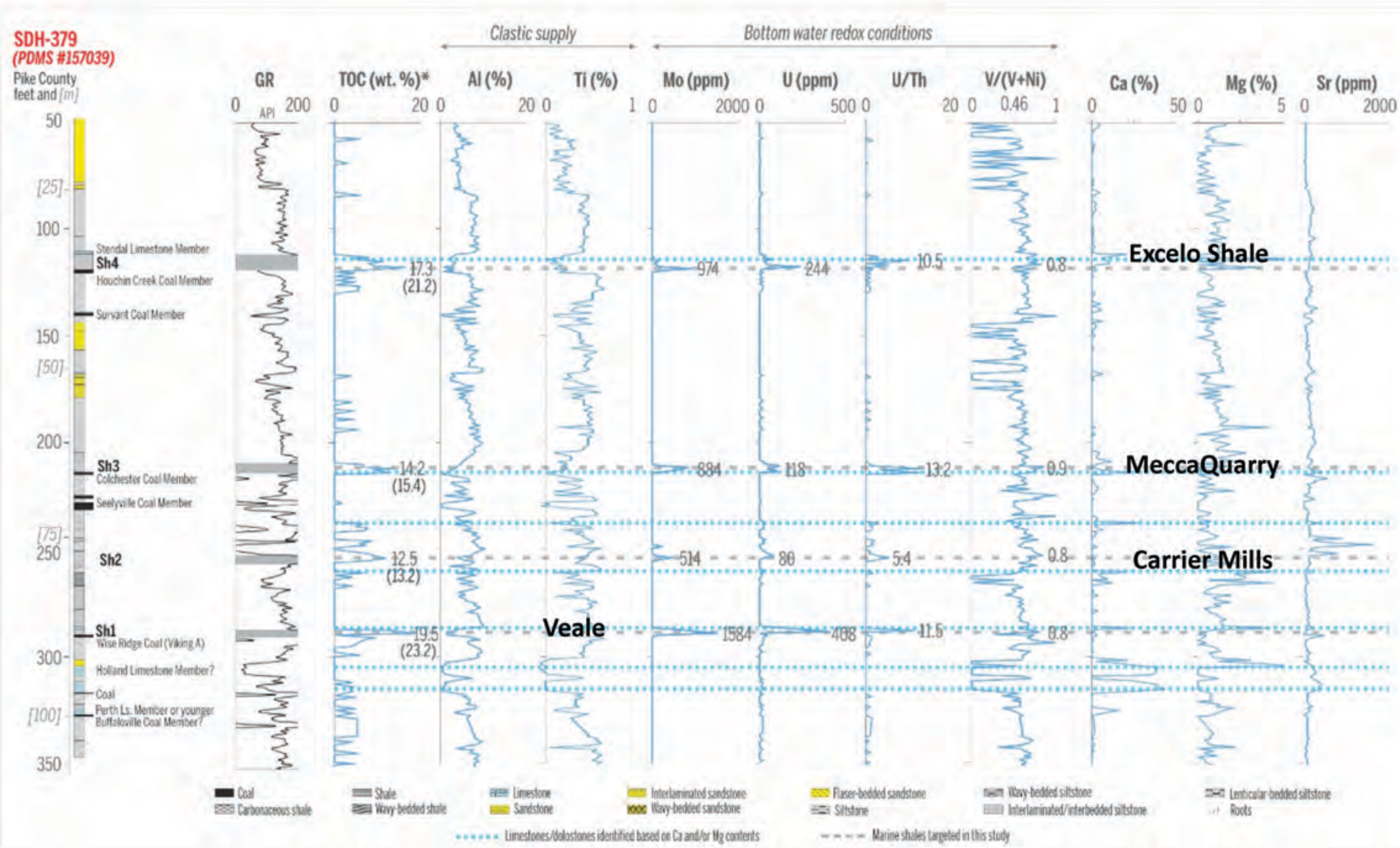
In this classification, critical elements include Nd, Eu, Tb, Dy, Y, and Er; uncritical elements include La, Pr, Sm, and Gd; and Ce, Ho, Tm, Yb, and Lu are regarded as excessive elements.

The parameter known as the "outlook coefficient" (Coutl) is calculated as Coutl = (Nd + Eu + Tb + Dy+ER + Y/SumREY)/(Ce + Ho + TM + Yb + Lu/Sum REY); the higher the Coutl value, the more promising the ore with respect to potential industrial value.



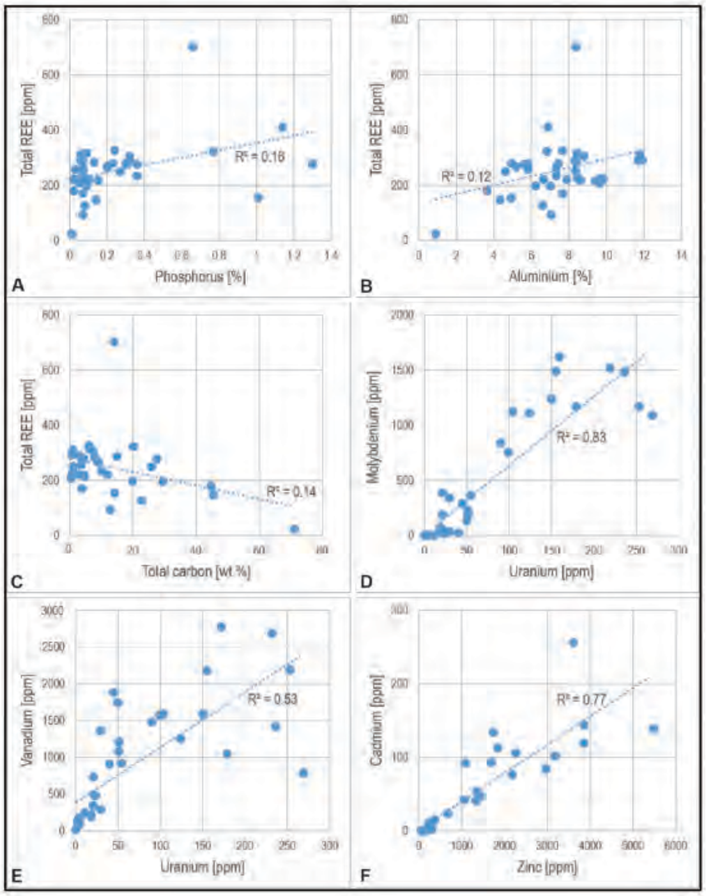


OTHER SELECTED ELEMENTS OF BLACK SHALES
Molybdenum [ppm]
2000
1500
1000
500
0
Zinc [ppm]
6000
4000
2000
0
Vanadium [ppm]
3000
2000
1000
0
Uranium [pmm]
300
200
100
0
Cadmium [ppm]
300
200
100
0
Arsenic [ppm]
250
200
150
100
50
0
Anna Shale
Turner Mine Shale
Excello Shale
Mecca Quarry Shale
Carrier Mills Shale
Veale Shale
Other Shales
UCC
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY



From Mastalerz et al., 2019

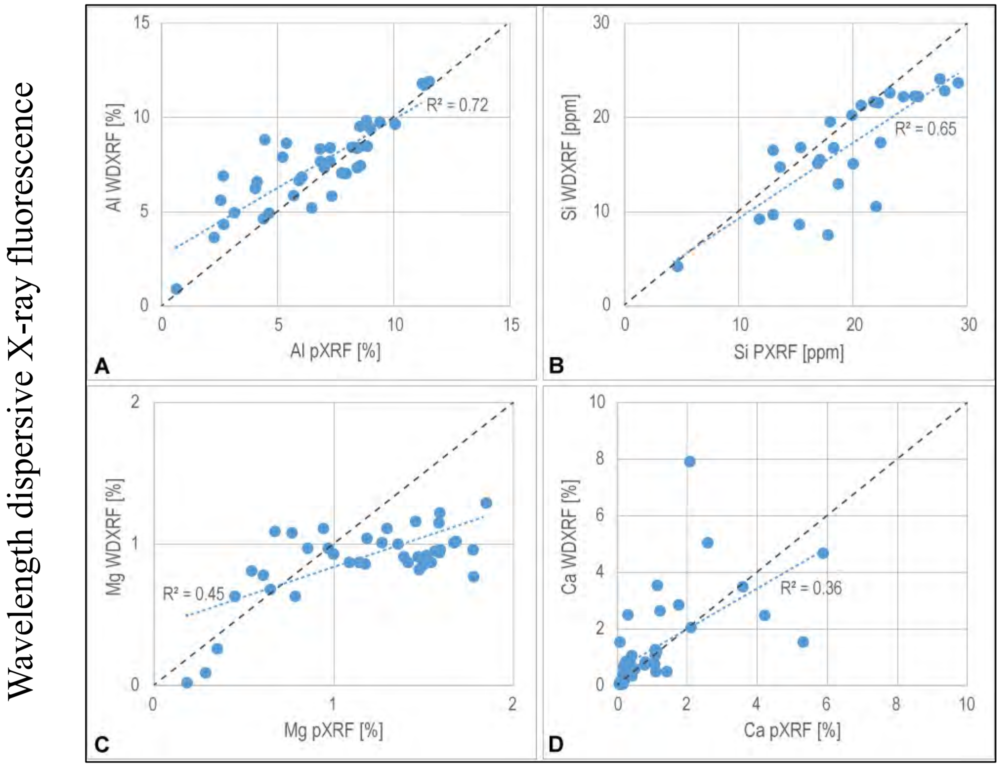
ASSOCIATIONS of CRITICAL ELEMENTS OF BLACK SHALES



- weak positive correlation of REE with P and Al
- weak negative correlation of REE with TC
- Mo, V, and U – positive correlations with one another – organic association?
- Cd positively correlated with Zn – hydrothermal influence?

INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

COMPARING pXRF AND WDXRF ELEMENTAL COMPOSITION



INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

CONCLUSIONS

1) In marine shales, Mo and V concentrations are very high, at places exceeding 1000 ppm for Mo and 1600 for V. Among the six marine shales studied, the Mecca Quarry Shale is the richest in Mo (average 1103.8 ppm) and V (1605 ppm), followed by the Veale Shale and the Excello Shale, making them all valuable sources for these elements. In the non-marine shales, the concentration of Mo and V are low, only slightly above the values in the UCC.

2) The marine shales studied are highly enriched in concentrations of Zn, As, and Cd. The Mecca Quarry Shale is the most enriched in Zn, with some samples having more than 5000 ppm. Considering 70 ppm as the value for the UCC, the Excello Shale and the Veale Shale also have Zn concentrations more than ten times higher. Arsenic content is the highest in the Veal Shale, averaging 61.7 ppm, with some samples reaching more than 200 ppm, which is also highly enriched compared to 1.8 ppm in UCC.

INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

CONCLUSIONS

3) Concentrations of REE in the shales ranged from 231 to 701.8 ppm. Together with the previous data on Pennsylvanian shales showing a similar range, these values place below the 1000 ppm threshold to be considered a viable resource for REE. Although more research must be done on the associations and distribution controls in these organic-matter-rich marine black shales, our data suggest that REE are hosted by multiple fractions. This, in turn, suggests that significant efforts and resources would be needed to preconcentrate REE and ultimately make such shales a viable REE resource.

4) Being part of the Pennsylvanian cyclothems, marine black shales often directly overlie coals, and we suggest that paleosol-coal-marine shale sequences could be jointly considered as a resource for selected critical minerals. There are numerous locations where these three lithologies add to significant thickness and are available at a shallow depth.

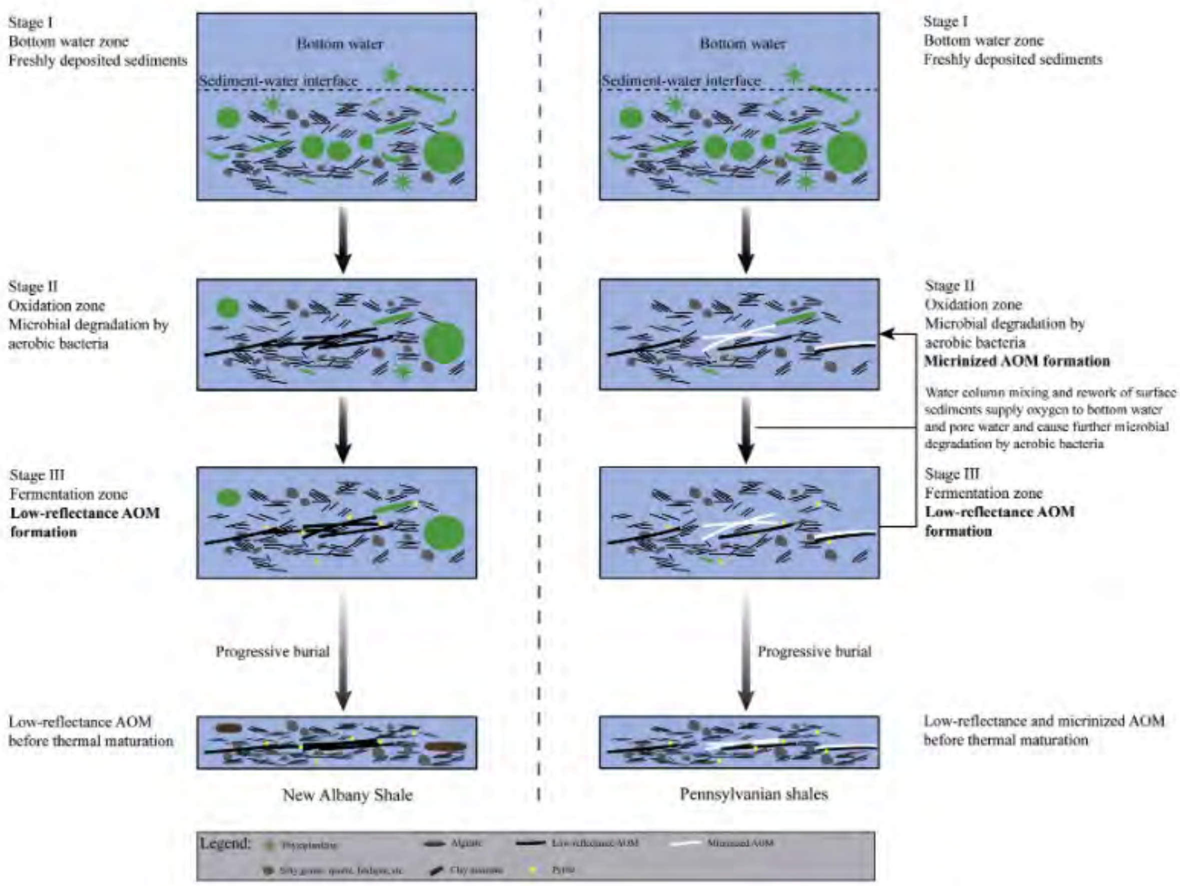
INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

List of critical minerals

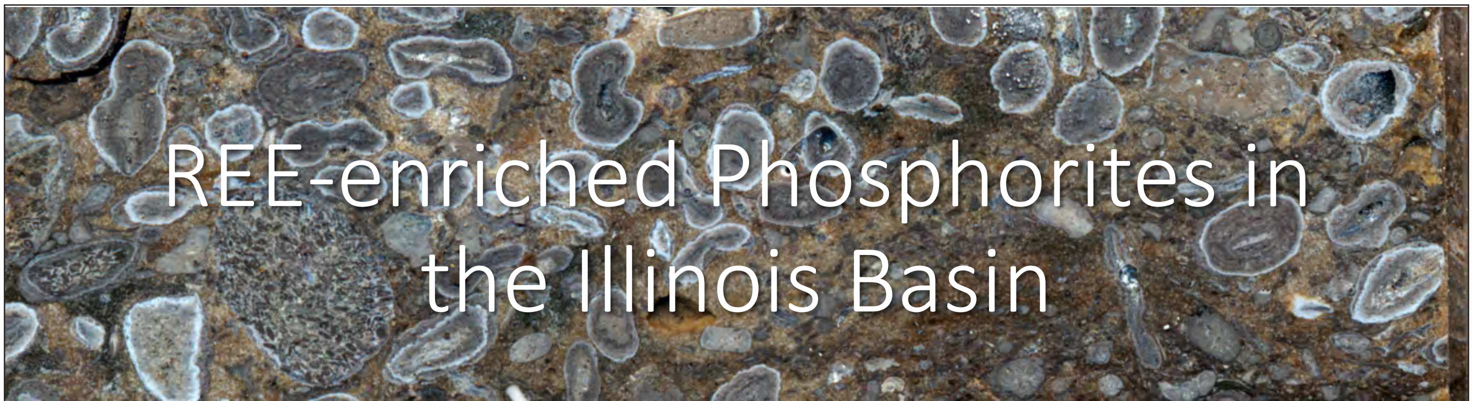
- Aluminum, used in almost all sectors of the economy
- Antimony, used in lead-acid batteries and flame retardants
- Arsenic, used in semi-conductors
- Barite, used in hydrocarbon production.
- Beryllium, used as an alloying agent in aerospace and defense indus
- Bismuth, used in medical and atomic research
- Cerium, used in catalytic converters, ceramics, glass, metallurgy, ar
- Cesium, used in research and development
- Chromium, used primarily in stainless steel and other alloys
- Cobalt, used in rechargeable batteries and superalloys
- Dysprosium, used in permanent magnets, data storage devices, and
- Erbium, used in fiber optics, optical amplifiers, lasers, and glass col
- Europium, used in phosphors and nuclear control rods
- Fluorspar, used in the manufacture of aluminum, cement, steel, gas
- Gadolinium, used in medical imaging, permanent magnets, and ste
- Gallium, used for integrated circuits and optical devices like LEDs
- Germanium, used for fiber optics and night vision applications
- Graphite , used for lubricants, batteries, and fuel cells
- Hafnium, used for nuclear control rods, alloys, and high-temperatu
- Holmium, used in permanent magnets, nuclear control rods, and la
- Indium, used in liquid crystal display screens
- Iridium, used as coating of anodes for electrochemical processes and as a chemical catalyst
- Lanthanum, used to produce catalysts, ceramics, glass, polishing compounds, metallurgy, and batteries
- Lithium, used for rechargeable batteries
- Lutetium, used in scintillators for medical imaging, electronics, and some cancer therapies
- Magnesium, used as an alloy and for reducing metals
- Manganese, used in steelmaking and batteries
- Neodymium, used in permanent magnets, rubber catalysts, and in medical and industrial lasers
- Nickel, used to make stainless steel, superalloys, and rechargeable batteries
- Niobium, used mostly in steel and superalloys
- Palladium, used in catalytic converters and as a catalyst agent
- Platinum, used in catalytic converters
- Praseodymium, used in permanent magnets, batteries, aerospace alloys, ceramics, and colorants
- Rhodium, used in catalytic converters, electrical components, and as a catalyst
- Rubidium, used for research and development in electronics
- Ruthenium, used as catalysts, as well as electrical contacts and chip resistors in computers
- Samarium, used in permanent magnets, as an absorber in nuclear reactors, and in cancer treatments
- Scandium, used for alloys, ceramics, and fuel cells
- Tantalum, used in electronic components, mostly capacitors and in superalloys
- Tellurium, used in solar cells, thermoelectric devices, and as alloying additive
- Terbium, used in permanent magnets, fiber optics, lasers, and solid-state devices
- Thulium, used in various metal alloys and in lasers
- Tin, used as protective coatings and alloys for steel
- Titanium, used as a white pigment or metal alloys
- Tungsten, primarily used to make wear-resistant metals
- Vanadium, primarily used as alloying agent for iron and steel
- Ytterbium, used for catalysts, scintillometers, lasers, and metallurgy
- Yttrium, used for ceramic, catalysts, lasers, metallurgy, and phosphors
- Zinc, primarily used in metallurgy to produce galvanized steel
- Zirconium, used in the high-temperature ceramics and corrosion-resistant alloys.

INDIANA GEOLOGICAL & WATER SURVEY | INDIANA UNIVERSITY

Formation of amorphous organic matter in black shales



From Teng et al., 20



REE-enriched Phosphorites in the Illinois Basin

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Pat McLaughlin

USGS
science for a changing world

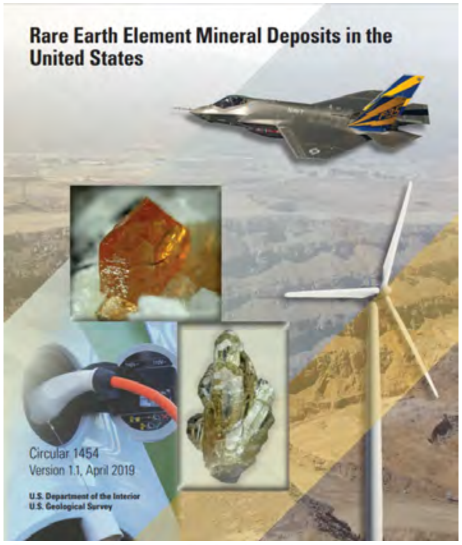
Contributors

Jared Freiburg (ISGS)
Jay Zambito (Beloit College)
Charles Ver Straeten (NYGS)
Alex Bartholomew (SUNY New Paltz)
Drew Andrews (KGS)
Jed Day (IL State U.)
Mike Sell (Illinois State U.)
Erika Danielsen (OGS)
Jeff Trop (Bucknell U.)
Jeff Over (SUNY Geneseo)
Maria Mastalerz (IGWS)
Arkansas Geo. Survey
Oklahoma Geo. Survey
Matt Johnson (IGWS)

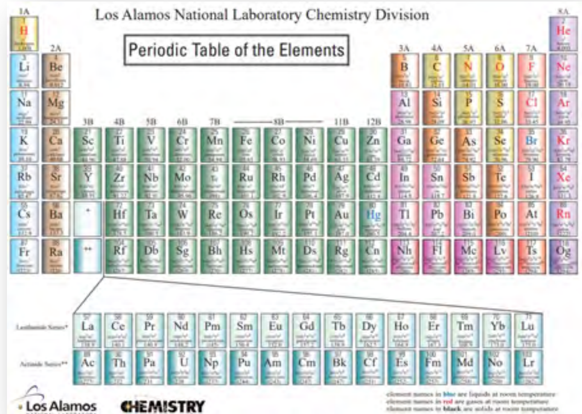
Poul (Emsbo)
Neil Griffis (USGS)
Ryan Clark (IGS)
Joe Devera (ISGS)
Carlton Brett (U. Cincinnati)
Gordon Baird (SUNY Fredonia)
Ron Clendening (TGS)
Katherine Tucker (IGWS)
Greg Cane (ISGS)
Dave Malone (IL State U.)
Damon

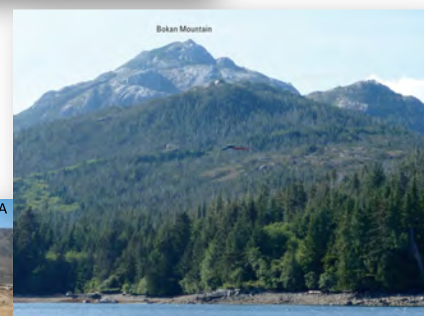
Thijs Vandenbroucke (U. Ghent, Belgium)
Jahan Ramezani (MIT)
Alyssa Bancroft (IGS)
Tim Paton (ISGS)
Cristiana Esteves (U. Ghent)
Kyle Ganz (MGS)
Bill Batten (WGNHS)
Carsyn Ames (WGNHS)
Jenna Lanman (IGWS)
Brian Witzke (IGS)
Heikki Bauert (Estonian GS)
Jared Thomas (ISGS)

EMRI: REEs

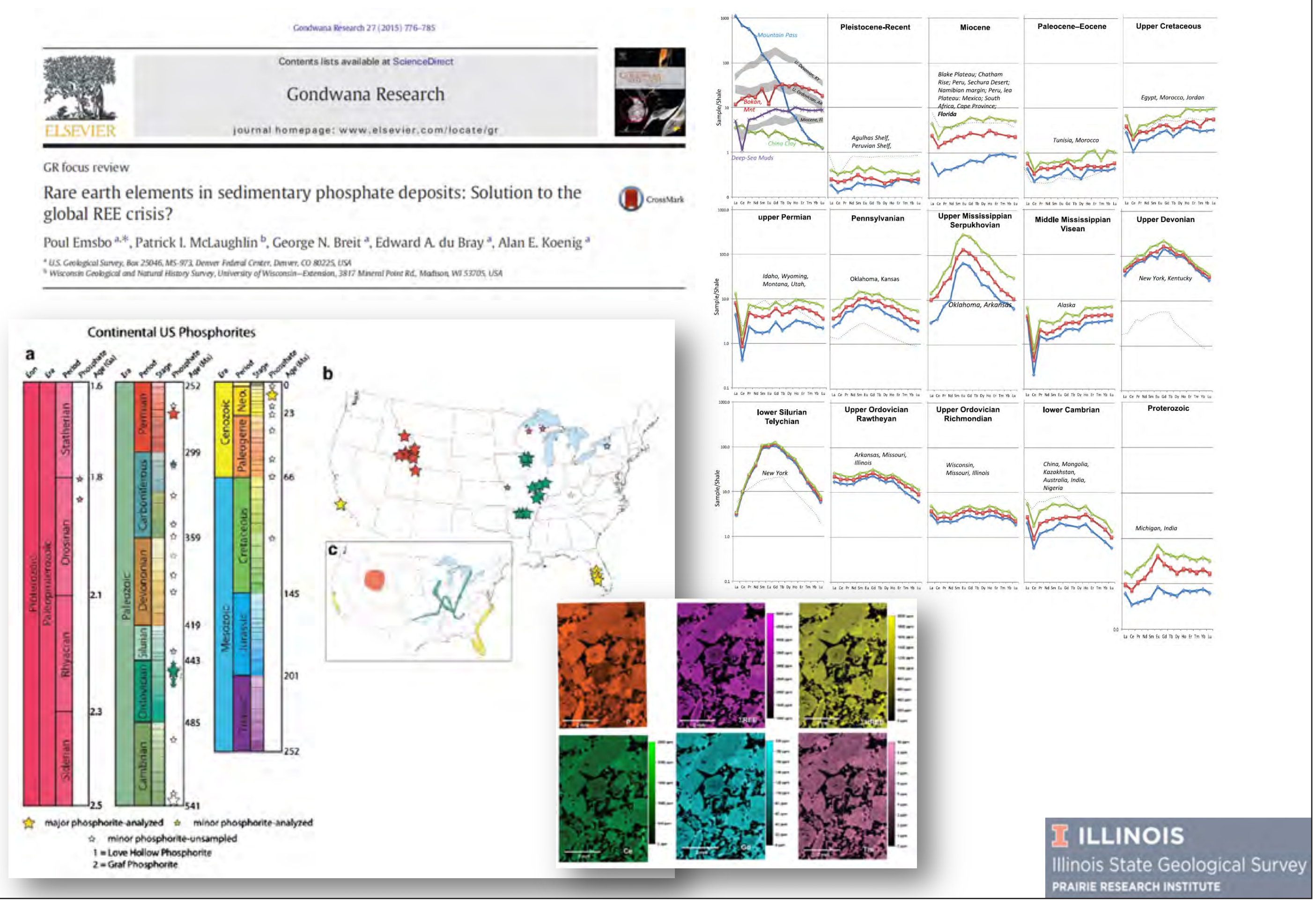


By Bradley S. Van Gosen, Philip L. Verplanck, and Poul Emsbo



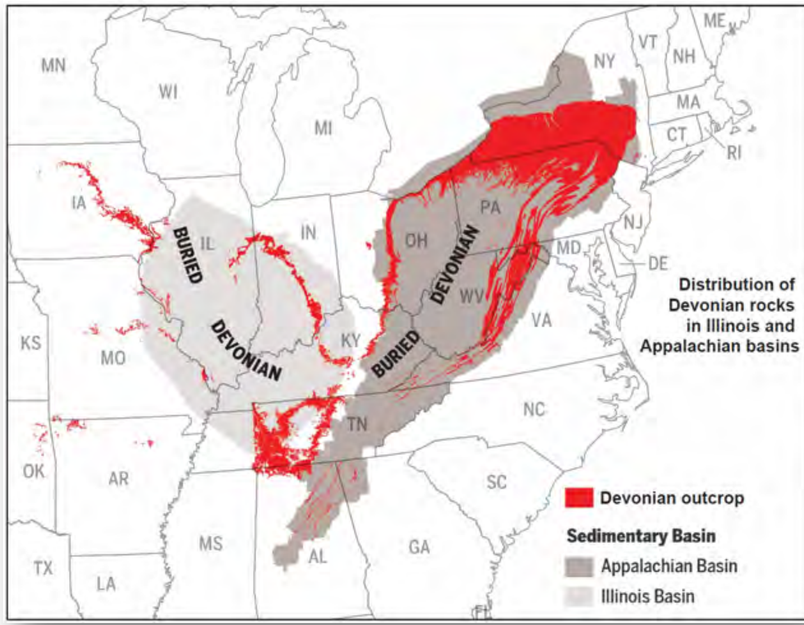


Sedimentary phosphate REEs



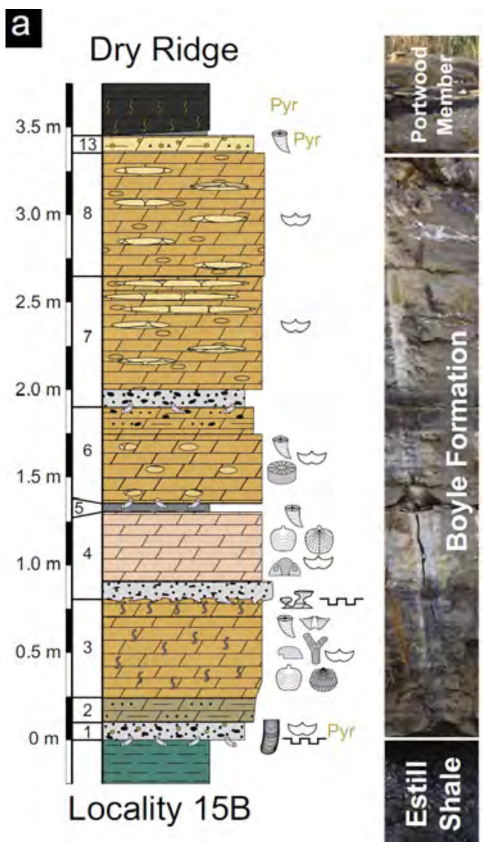
Earth MRI Phase II: Geochemical Sampling (Appalachian Basin) and Regional Interpretation (Illinois and Appalachian Basins) of Devonian-Aged Rare Earth Element-Enriched Sedimentary Phosphatic Stratigraphic Units in the Central and Eastern United States

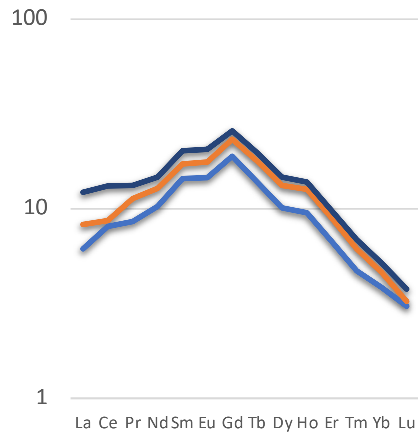
- Appalachian Basin
  - New York
  - Pennsylvania
  - West Virginia
  - Ohio
  - Kentucky
- Illinois Basin
  - Indiana
  - Illinois
  - Kentucky
  - Tennessee
  - Iowa
  - Missouri
  - Arkansas
  - Oklahoma

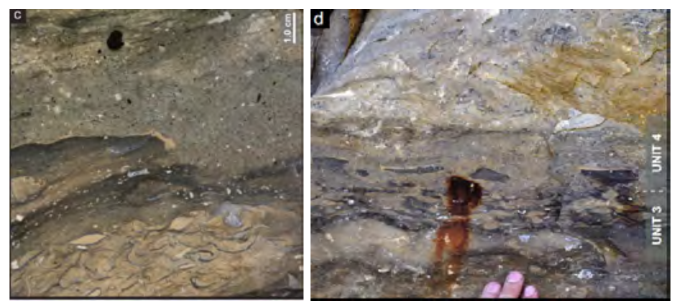


ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Midcontinent Devonian phosphorite: Kentucky







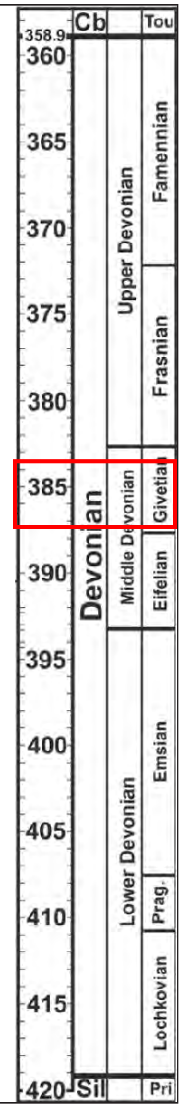

Palaeobiodiversity and Palaeoenvironments (2018) 98:331–368
https://doi.org/10.1007/s12549-018-0323-6

SENCKENBERG

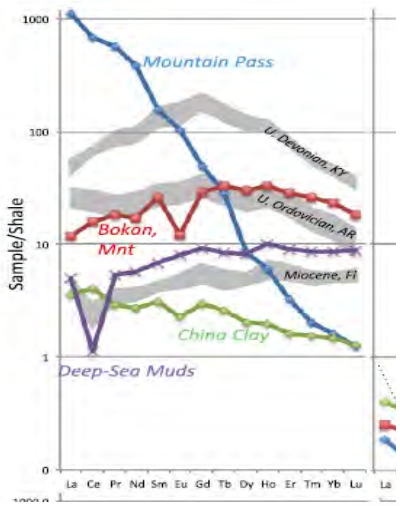
ORIGINAL PAPER

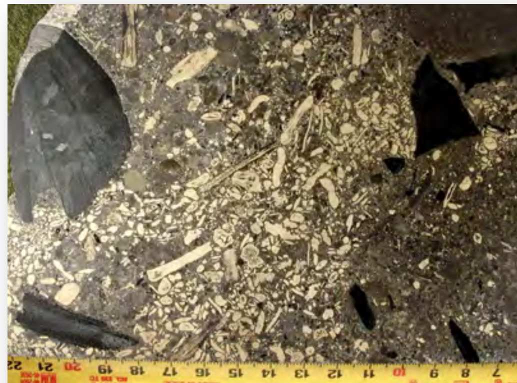
Litho-, bio-, and sequence stratigraphy of the Boyle-Portwood Succession (Middle Devonian, Central Kentucky, USA)

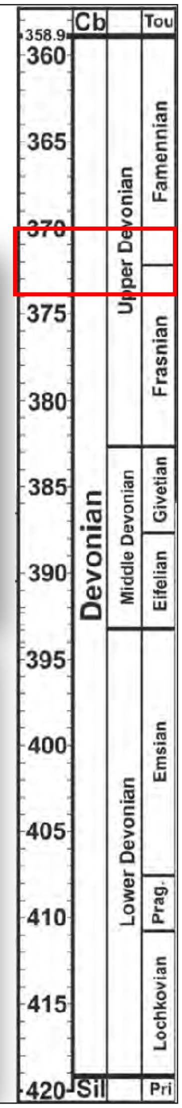
Carlton E. Brett[1] · James J. Zambito IV[2] · Gordon C. Baird[3] · Z. Sarah Aboussalam[4] · R. Thomas Becker[4] · Alexander J. Bartholomew[5]



Midcontinent Devonian phosphorite: Kentucky

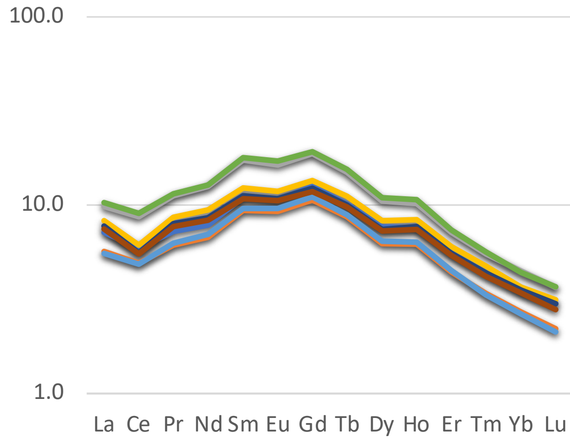


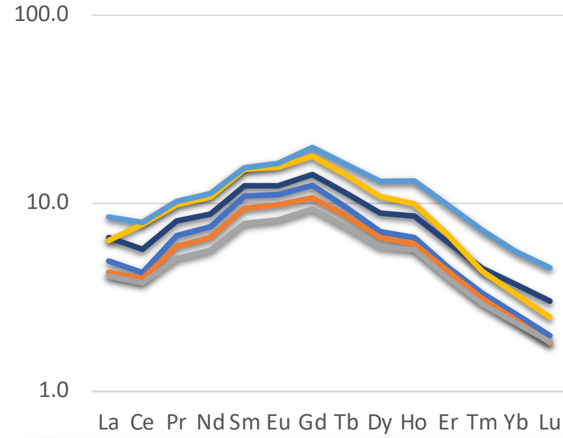


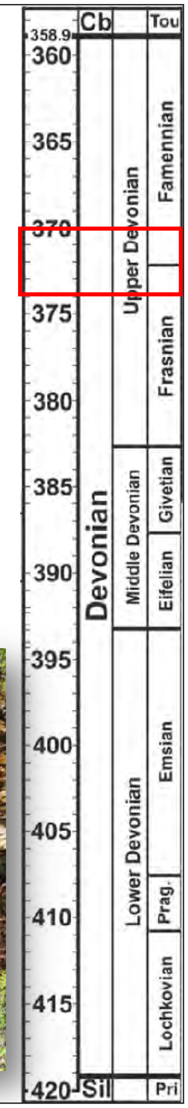


Midcontinent Devonian phosphorite:

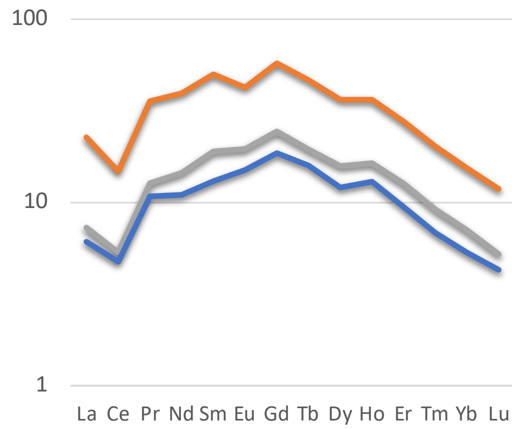
Tennessee

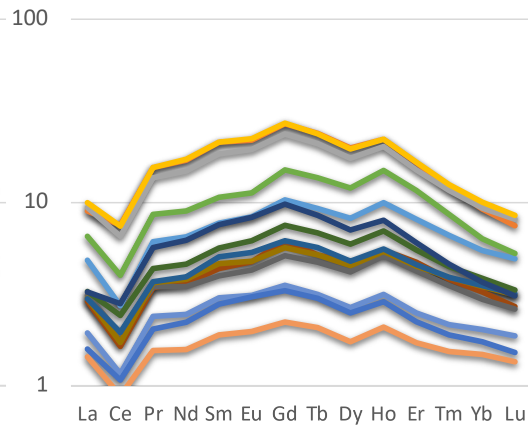


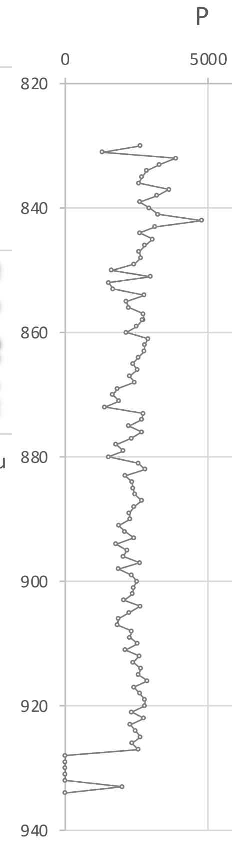


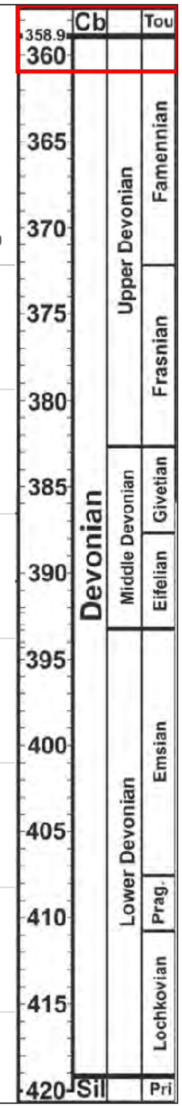


Midcontinent Devonian-Miss. phosphorite:
Kentucky + Indiana

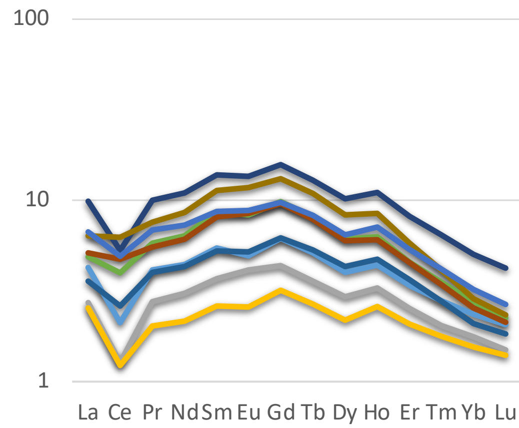


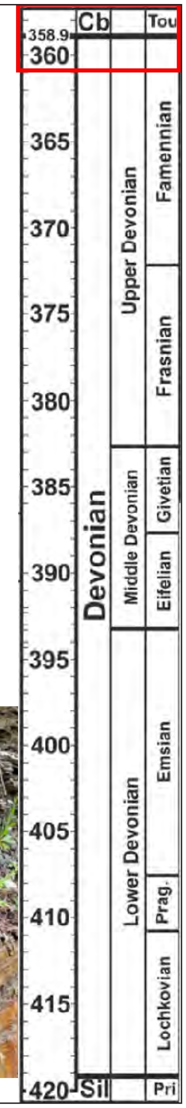




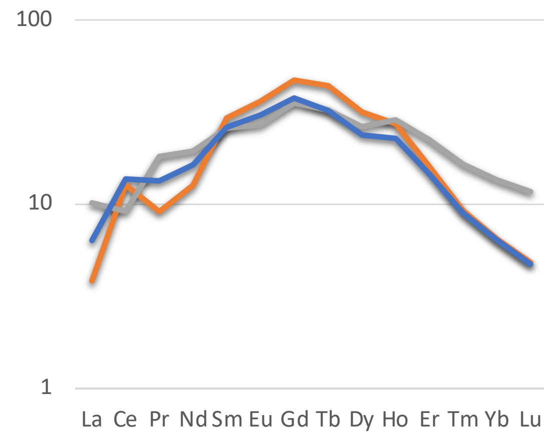


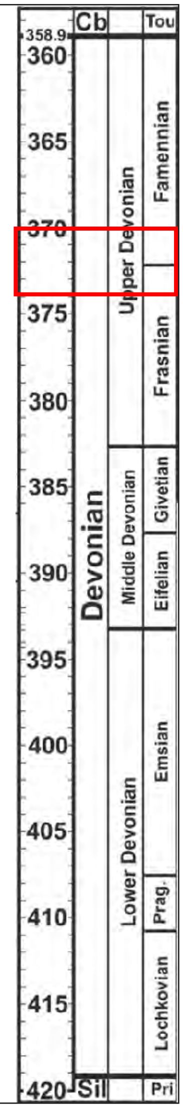
Midcontinent Devonian-Miss. phosphorite:
Tennessee





Midcontinent Devonian-Miss. phosphorite: Illinois

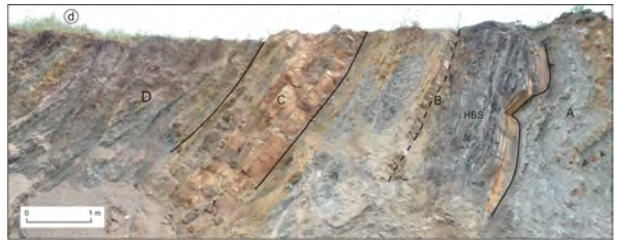




Association with Devonian oceanic anoxic events

Hangenberg Event

- Devonian-Mississippian boundary (359 Ma)
- 2nd largest extinction in Devonian
- Large carbon isotope excursion (+5 per mil)
- Widespread black shales-oceanic anoxia



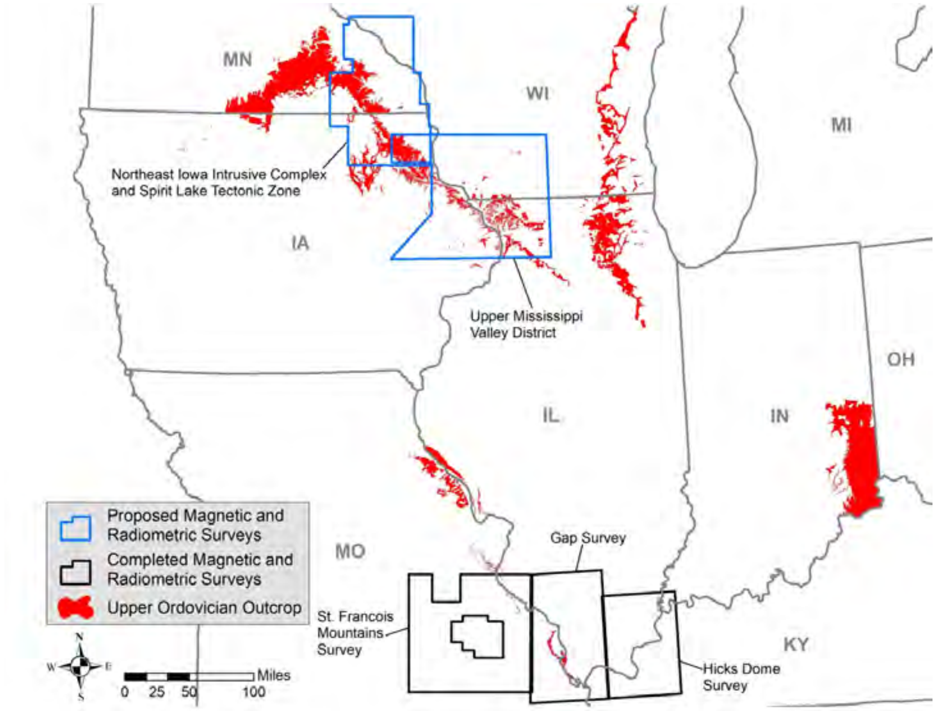
Hangenberg black shale, Kowala Quarry, Poland (Matyja et al., 2021)

Kellwasser Event

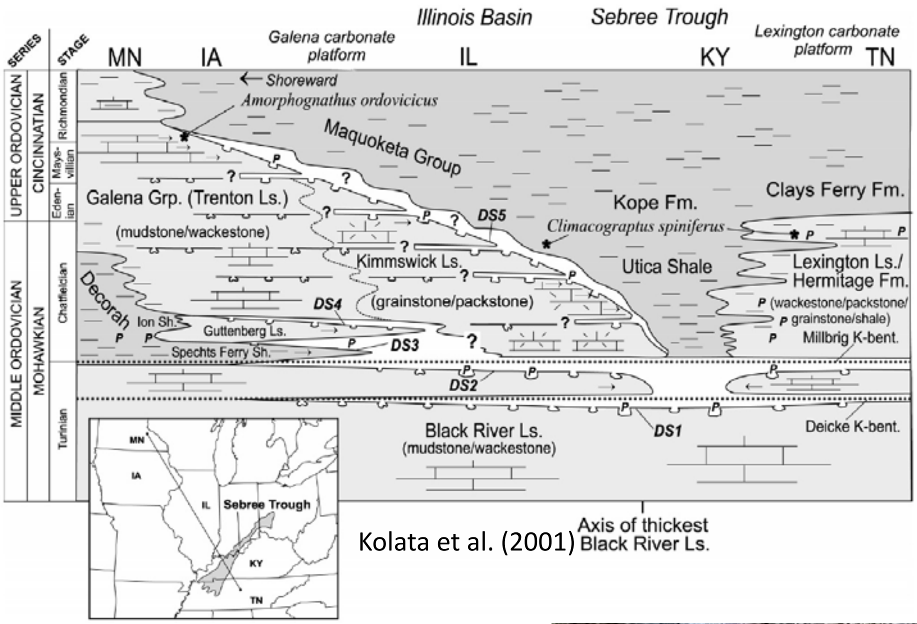
- Frasnian-Famennian boundary (372 Ma)
- One of top 5 largest mass extinction events
- Two pulses of oceanic anoxia

Earth Mapping Resources Initiative:

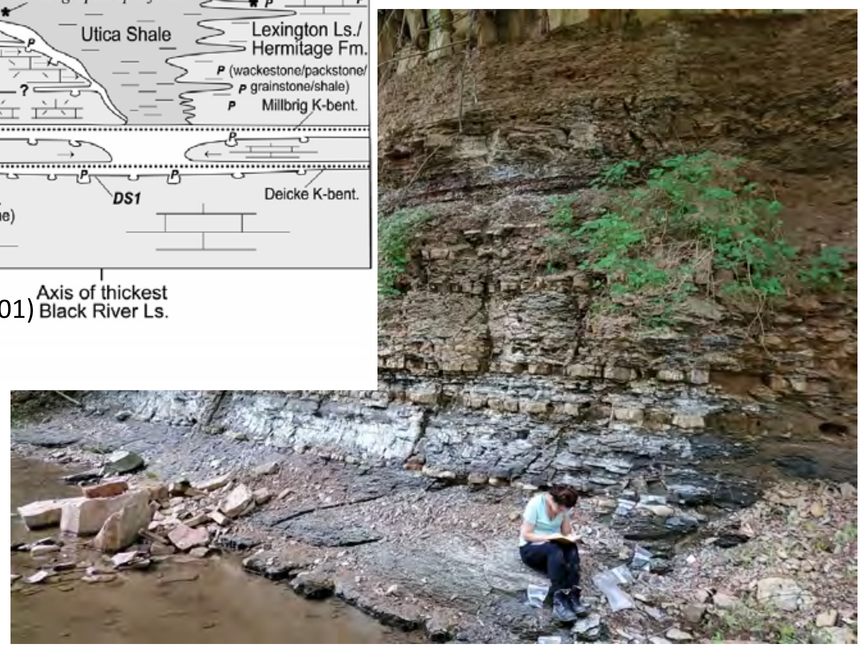
Geochemical Reconnaissance of Ordovician-aged Rare Earth Element-Enriched Sedimentary Phosphate in the Central United States



Regional stratigraphic framework

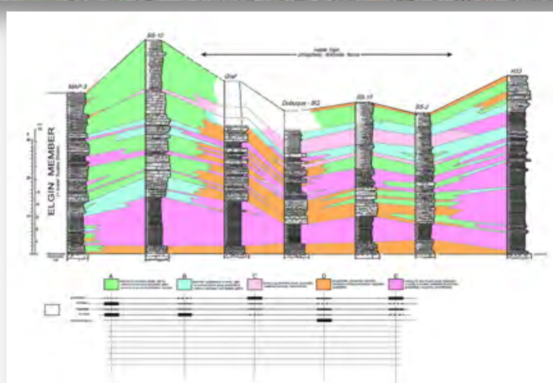


Kolata et al. (2001)



Midcontinent Ordovician phosphorite: *Graf Iowa*

Photo credit: B.J. Witzke

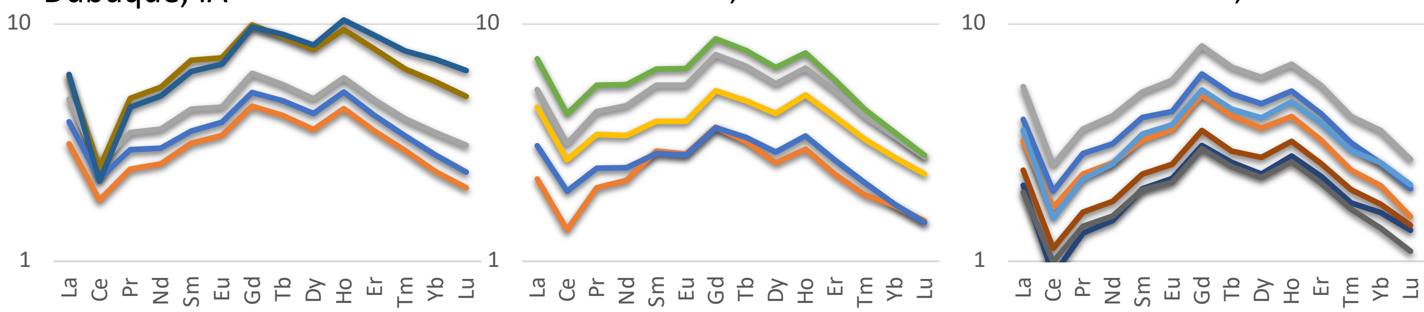


Ordovician phosphorite: *IA-WI-IL*

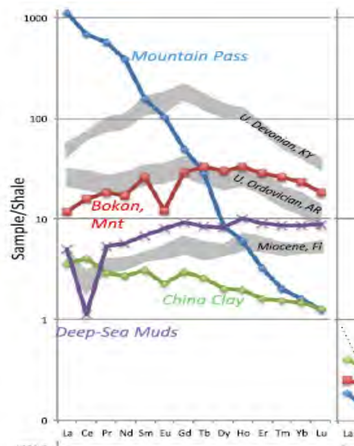
Browns Bottom Quarry
Dubuque, IA

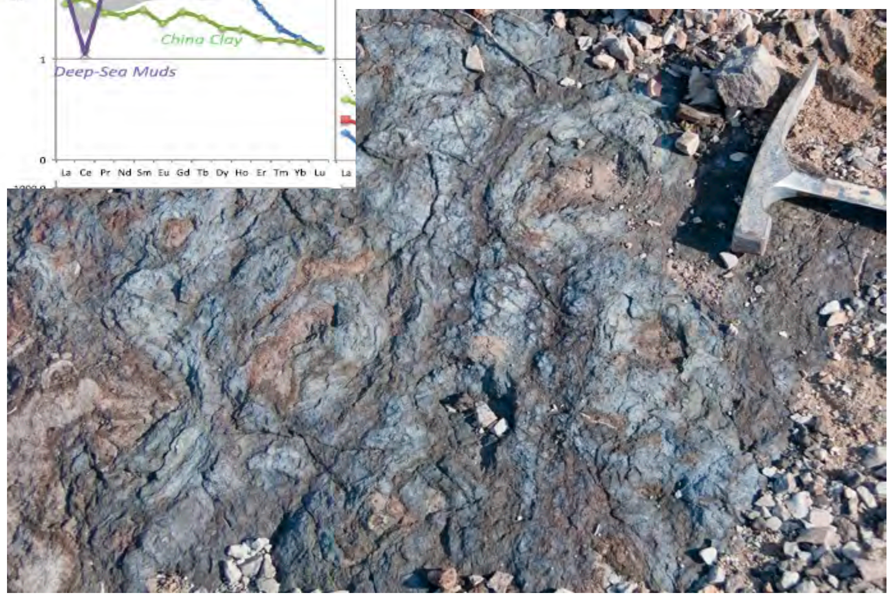
Mt. Carol Quarry
Mt. Carol, IL

Minooka Park core
Milwaukee, WI



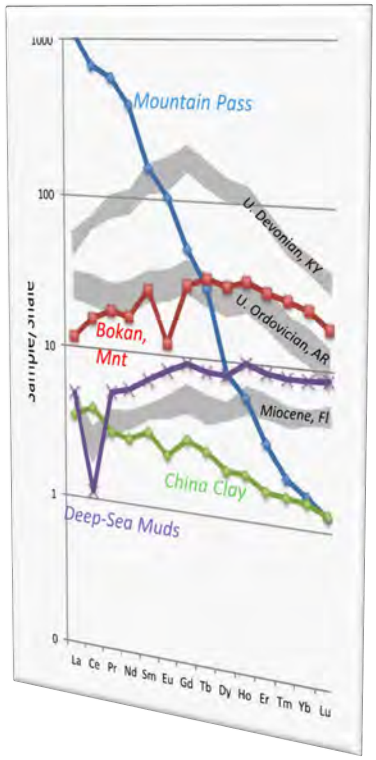
Ordovician phosphate and black shales: *Love Hollow phosphorite (Arkansas)*



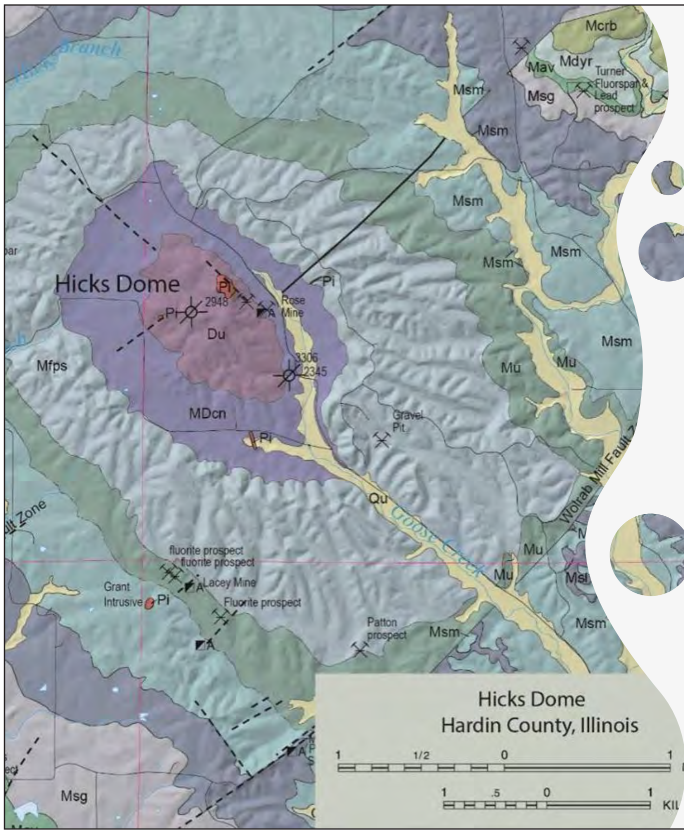


Summary

- Devonian phosphate REEs
  - Project is extended to June 2023
  - 230 samples analyzed so far
  - Results support preliminary findings
  - TN deposits show greatest potential
  - Stable isotope work planned
  - More work mapping deposits needed



- Ordovician phosphate REEs
  - Project still ramping up, runs until Sept. 2024
  - Hundreds of samples already submitted
  - Coordinated with PhD work on chitinozoan and graptolite biostrat
  - Fledgling geochronology effort underway
  - Regional chemostratigraphy ramping up



Rare earth elements and critical minerals at Hicks Dome, Illinois

Jarek Trela, Illinois State Geological Survey
Jared Freiburg, Illinois State Geological Survey
Mingyue Yu, Illinois State Geological Survey
Kelly Rea Wilson, Illinois State Geological Survey

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

USGS
science for a changing world

Why should we care about rare earth elements and critical minerals?

-Electric vehicles

-Magnets

-Wind turbines

-Super-conductors

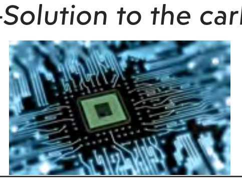
-Micro-chips

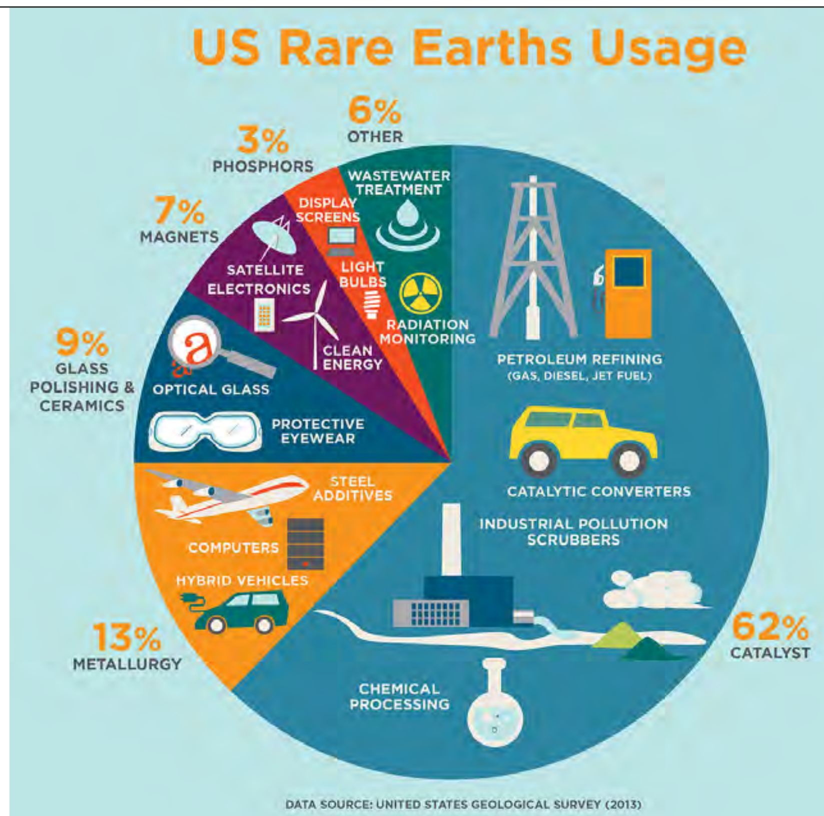
-Medical technology

-Screens/electronics/etc.

-National security technology

-Solution to the carbon/climate crisis



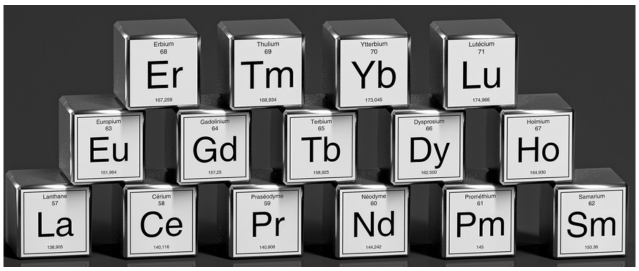


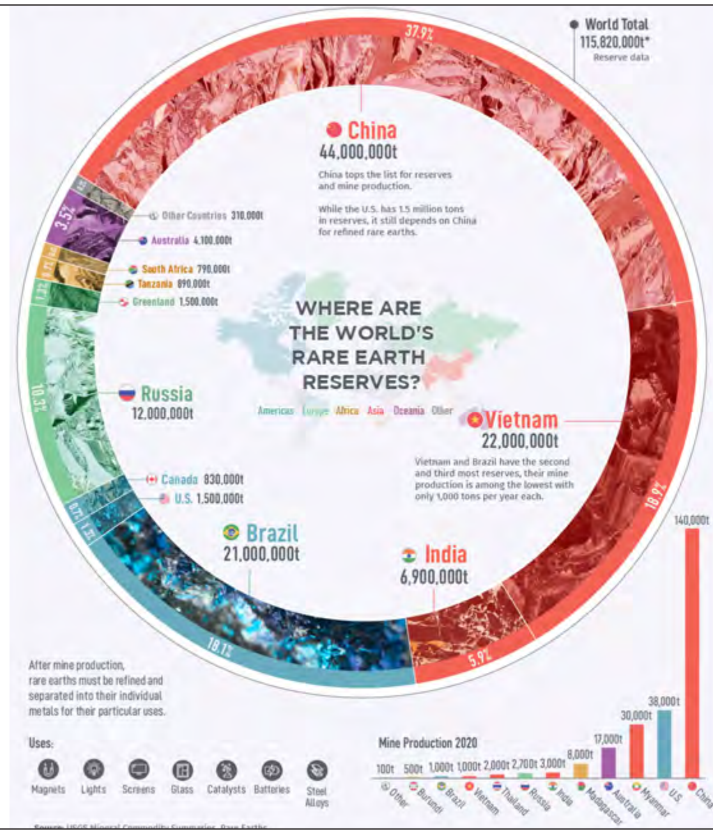
What are critical minerals and rare earth elements and where are they found?

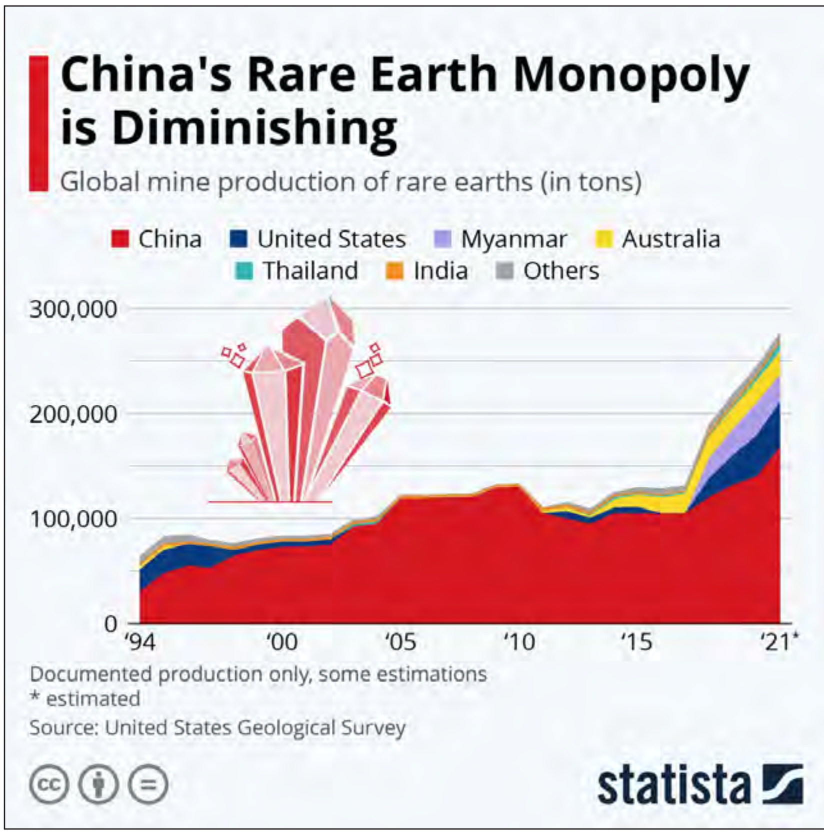
-Any element the federal government deems vital to economic and national security.

-Rare Earth Elements: lanthanide series of the periodic table (numbers 57-71)

-Sc and Y also included as REEs.







China has historically dominated the global REE industry producing over 90% of the global supply. However, there are signs of change.

In 2021 only 58% of REEs were produced in China.

The United States, Australia, and others account for the remaining 42%.

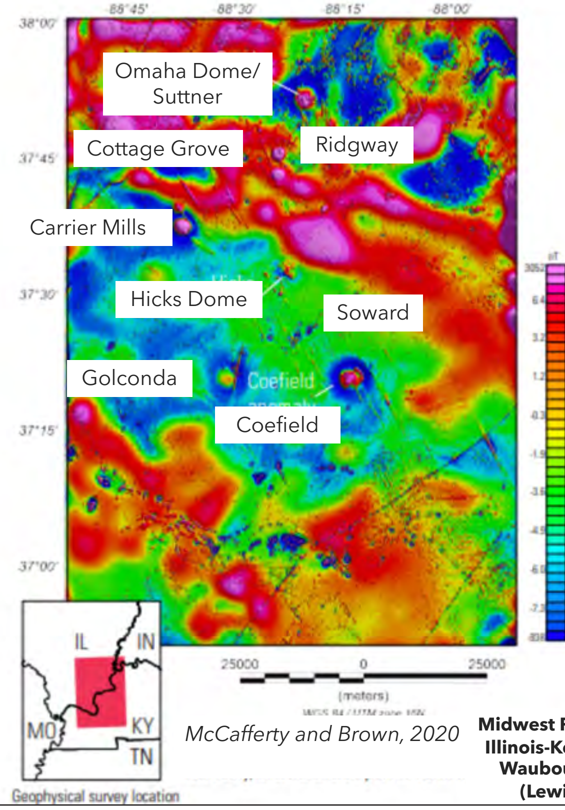
Continued investments, research, and exploration will help reduce the USA's dependence on foreign REE sources.

Mt. Pass (CA) remains the only open REE mine in the United States and produces largely LREE.

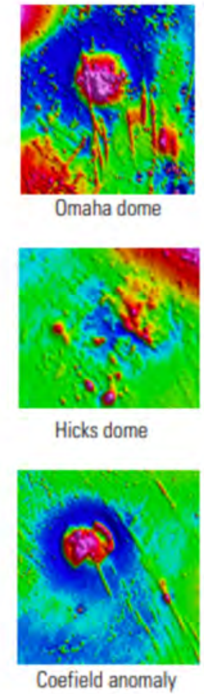
Hicks Dome potentially represents a viable HREE prospect.

USGS Earth Mapping Resources Initiative

The goal of Earth MRI is to improve our knowledge of the geologic framework in the United States and to identify areas that may have the potential to contain undiscovered critical mineral resources. Enhancement of our domestic mineral supply will decrease the Nation's reliance on foreign sources of minerals that are fundamental to our security and economy.

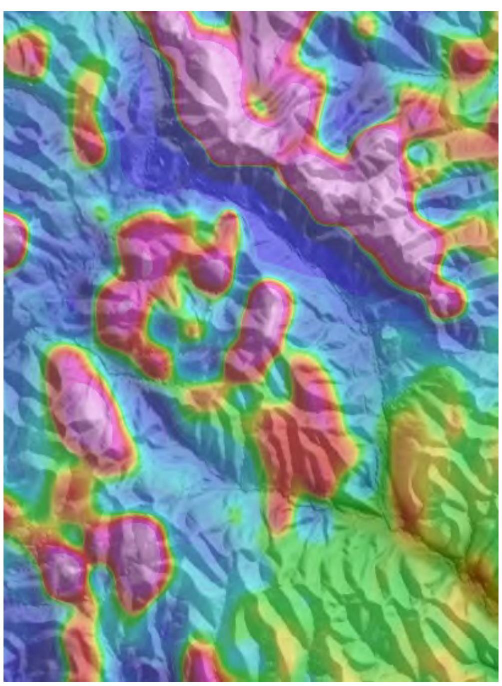


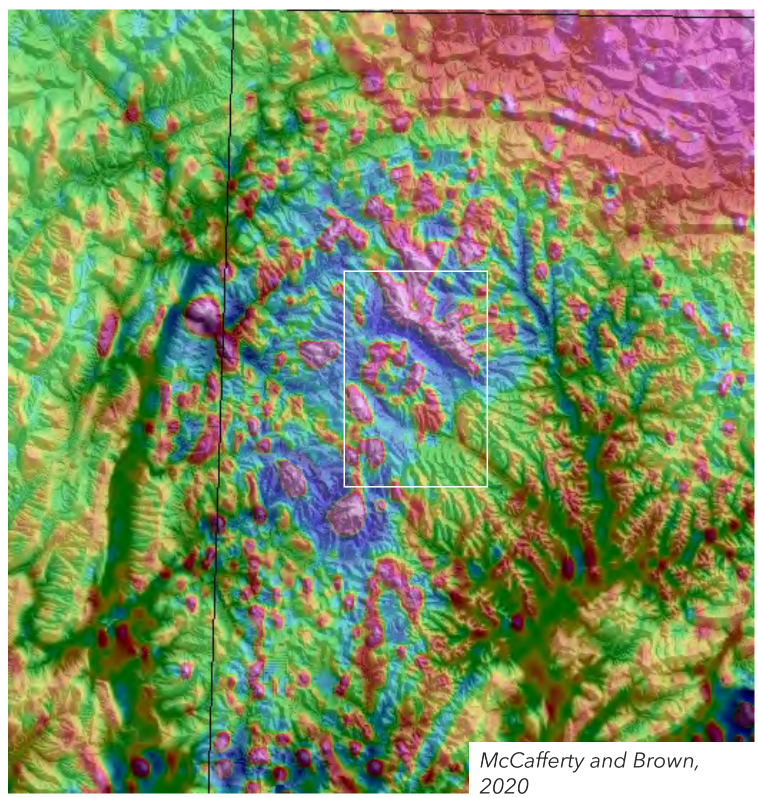
McCafferty and Brown, 2020



Midwest Permian Ultramafic District
Illinois-Kentucky Fluorspar District
Wauboukigou Alnöite Province
(Lewis and Mitchell, 1987)

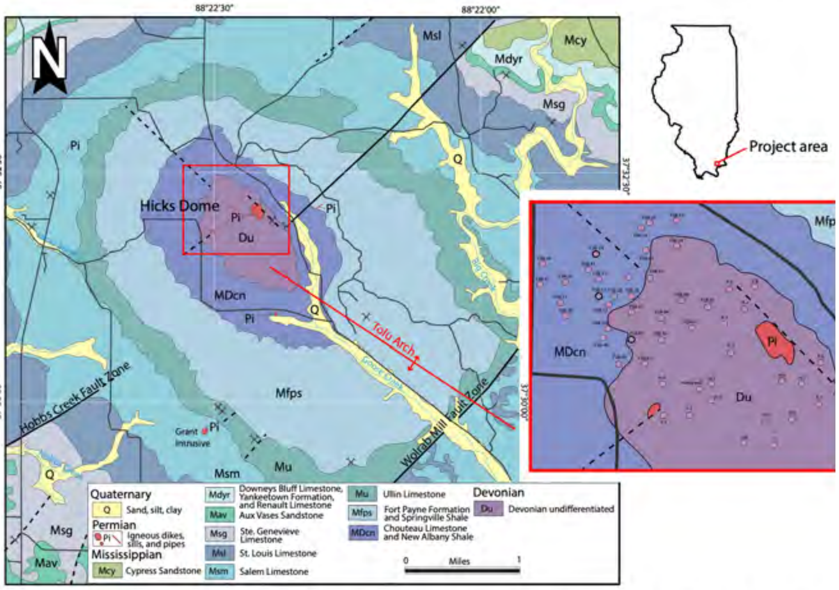
Hicks Dome, Hardin County Illinois
A magnetic anomaly is visible when data is reduced to the upper 140 m of the subsurface





McCafferty and Brown, 2020

History of resource and mineral exploration at Hicks Dome:



Denny et al., (2008, 2010)

1900s: Local fluorite mining. 99% of USA's production by 1914.

1935: Maretta Oil Company drills Hicks Dome looking for petroleum.

1971: Hicks Dome Corporation. 28 holes. >70,000 feet of drilling. Geochemical analysis.

1978: Asarco Inc. Continued exploration.

1994: Ozark Mahoning. Explores for fluorspar.

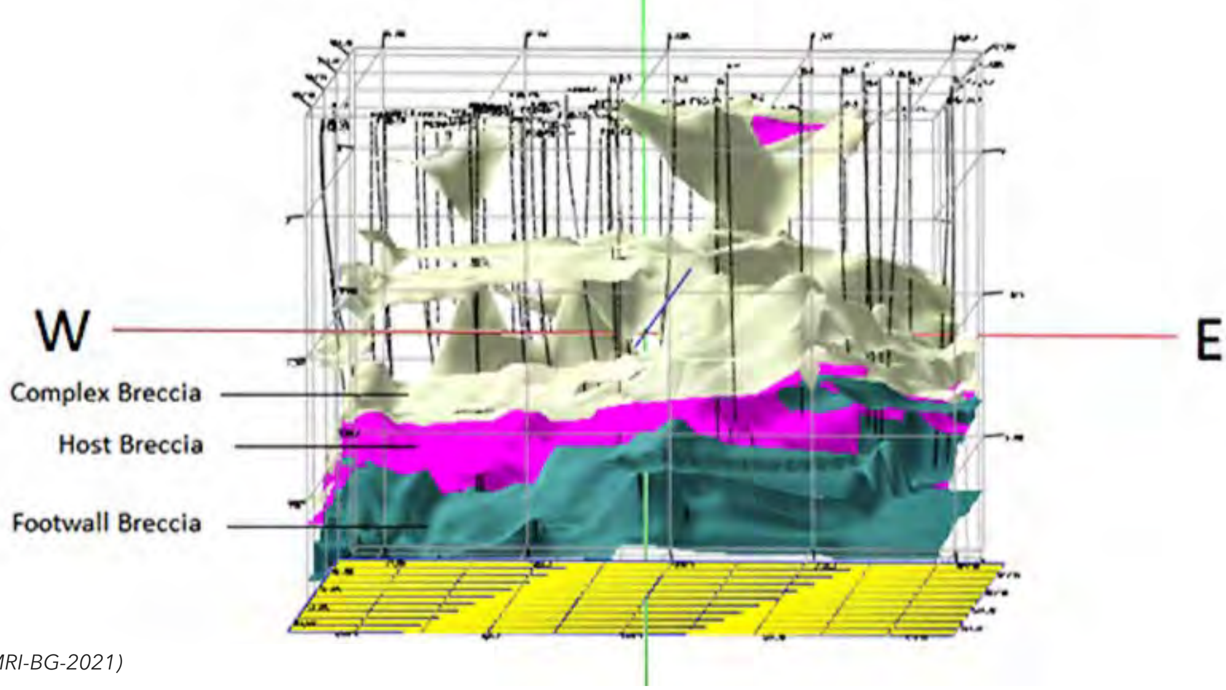
2005: Hicks Dome LLC. New owners.

2011: Great Western Minerals Group (Saskatchewan) looked at REE regolith.

Today: Hicks Dome LLC continues investigating the dome and attracting partners/investors. Schofield Engineering drill permit to look for oil down to granite?

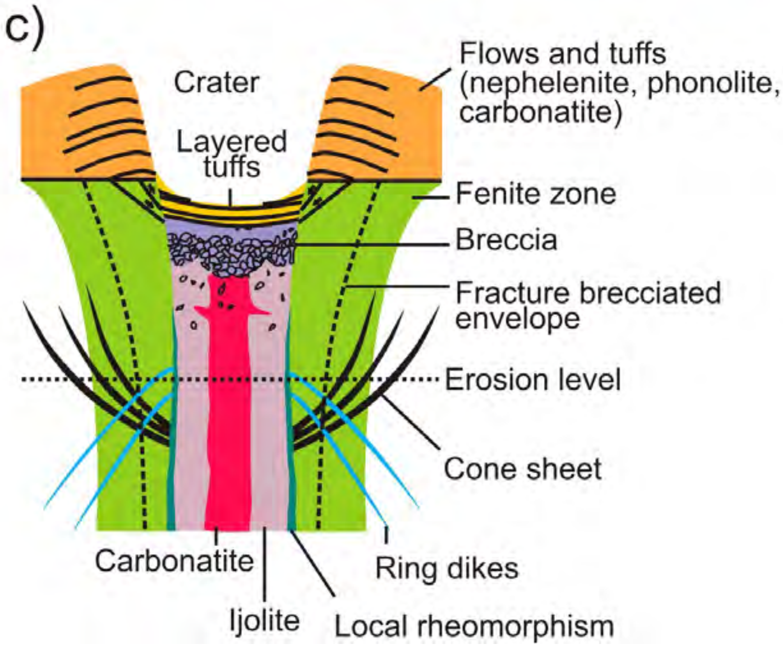
ISGS continues enhanced exploration of the dome

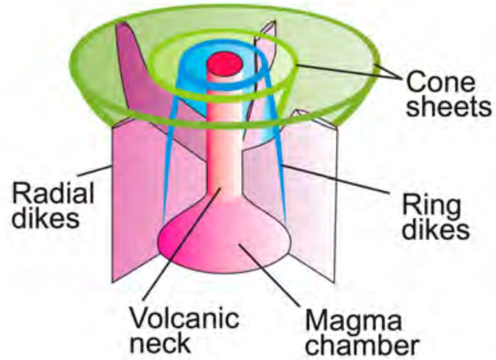
Cross-sectional (sub-surface view) through Hicks Dome



ISGS (Earth-MRI-BG-2021)

Morphology of carbonatite complexes as proposed by Sage and Watkinson (1991) to show convex and concave nature of ring dikes and cone sheets, respectively. This model provides a useful summary for exploration geology. Simandl and Pardis, 2018



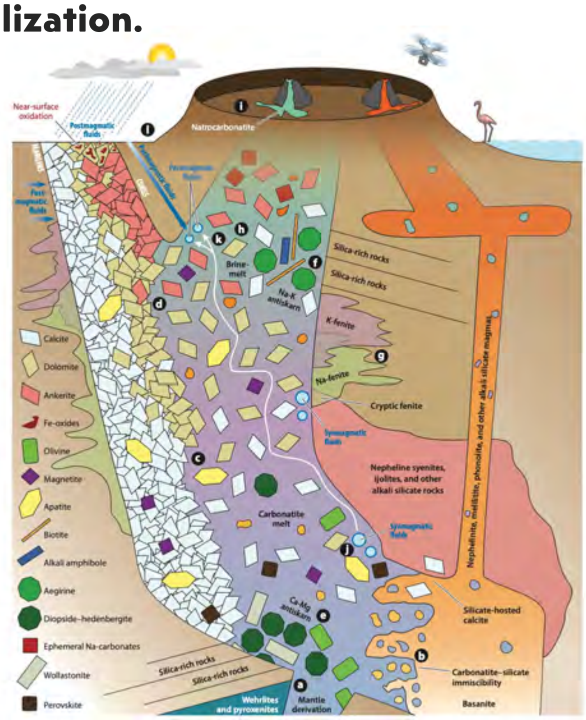


***Permian* igneous rocks in southern Illinois and western Kentucky provide an exceptional record to understand the link between carbonatites, carbonated-silicate melts, and rare earth element mineralization.**

How were carbonatites and associated lamprophyres in the Illinois Basin produced?

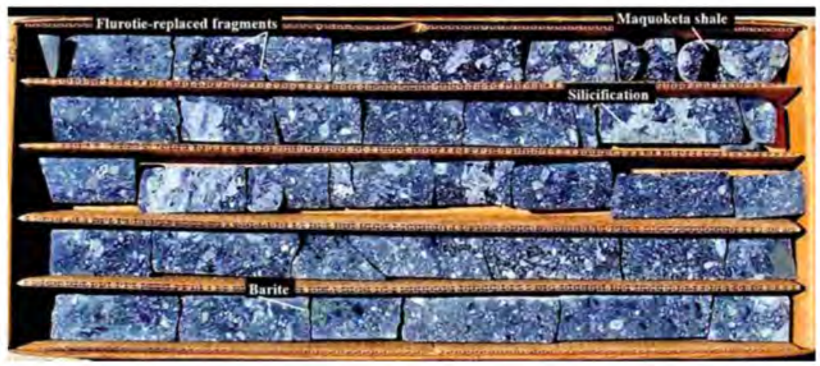
1. Primary carbonatite melt
2. Silicate-carbonatite immiscibility
3. Fractionation of silicate melt to produce carbonatite

Carbonatite and silicate magmas modified by fractional crystallization, reaction with wall rock, post-magmatic fluids, crustal assimilation, anti-skarnification



Yaxley et al., 2022

***Permian* rocks in Illinois consist of carbonatites, lamprophyres, and mineralized breccias (Hicks Dome). There are numerous fluorite mines surrounding the dome. Textures and rock relationships are complex and require careful examination.**



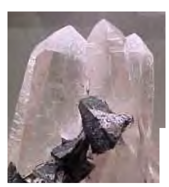
Critical minerals identified at Hicks Dome also occur in other carbonatite related prospects and deposits.

Fluorite: CaF_2
Barite: $BaSO_4$
F-Apatite: $Ca(PO_4)_3F$
Celestite: $SrSO_4$
Rutile, Anatase, Brookite: $(Ti, Nb)O_2$
Kobeite: $(Y, U)(Ti, Nb)_2(OH, F)_6$
Pyrochlore: $(Na, Ca, Pb, Y, U, REE)_2Nb_2O_6(OH)$ major site for Nd, Sm, Eu, Gd, Tb, Dy, Ho
Brabanite/Cheralite: $CaTh(PO_4)_2$
Britholite: $(Ce, Ca, Th, La, Nd)_5(SiO_4, PO_4)_3(OH, F)$
Xenotime: YPO_4 (2-10% Th_2O_5)
Monazite: $(Ce, La, Nd, Sm)PO_4$
Zircon: $ZrSiO_4$
Bertrandite: $Be_4(Si_2O_7)(OH)_2$
Helvite: $Be_3Mn_4(SiO_4)_5$
Synchisite: $Ca(Ce, La, Nd)(CO_3)_2F$
Parisite: $Ca(Ce, La)_2(CO_3)_3F_2$
Florencite: $(Ce, Sm)Al_3(PO_4)_2(OH)_6$
Bastnäsite: $(La, Ce, Y)CO_3F$

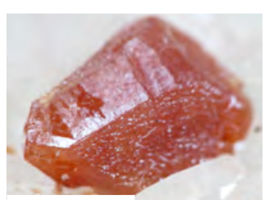
Denny et al., (2008, 2010) and
Hicks Dome LLC/Hagni Consulting LLC


Monazite


Xenotime


Helvite


Britholite


Florencite


Bastnäsite

Summary of calcining/leaching metallurgical test results – Hicks Dome

- Ubiquitous minerals include calcite, dolomite, fluorite, and quartz. Barite, celestite, and muscovite are present in all the samples. Sulphides and heavy minerals include pyrite, galena, sphalerite, and Nb-bearing rutile.
- REE-bearing minerals that were identified are apatite, pyrochlore, xenotime, and Th-phosphate.
- Mineral textures show that xenotime and Th-phosphate are in close association; the latter typically rims xenotime grains. The two phases are very fine-grained and occur along grain boundaries of the host minerals or in masses of fine grains in cracks or porous parts of muscovite.
- Apatite contains minor amounts of fine-grained xenotime.
- Pyrochlore is present as euhedral crystals.


Xenotime

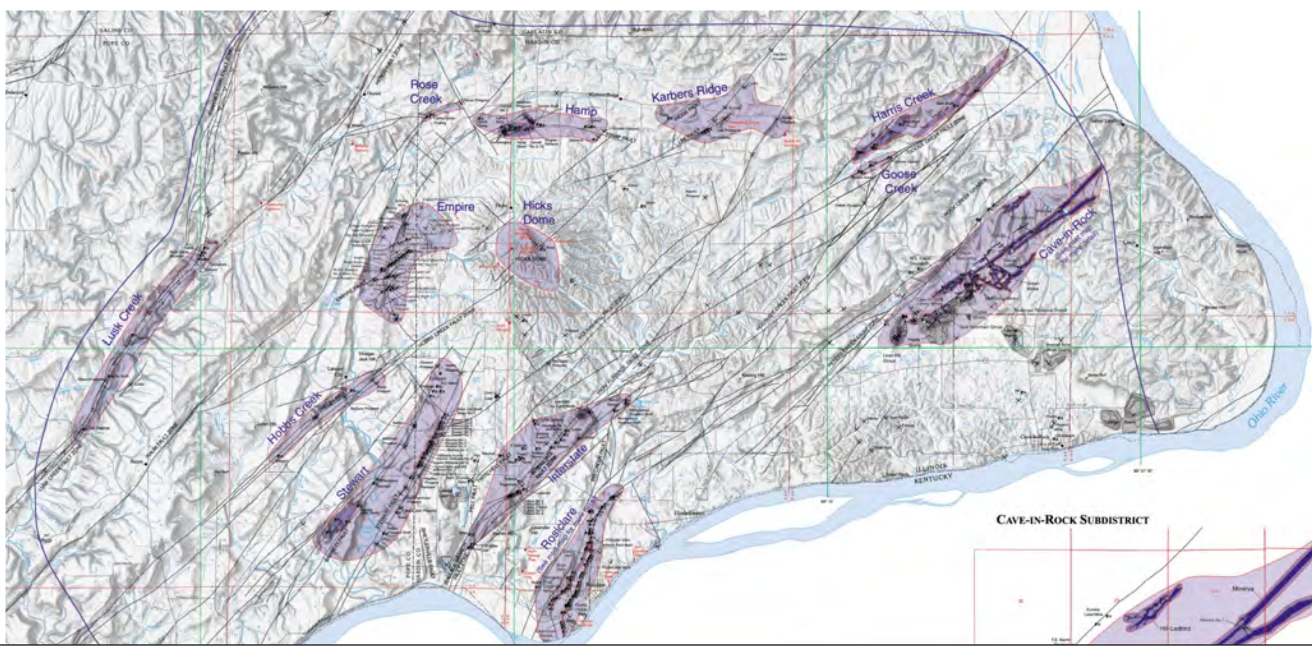

Fluorite


Apatite


Monazite

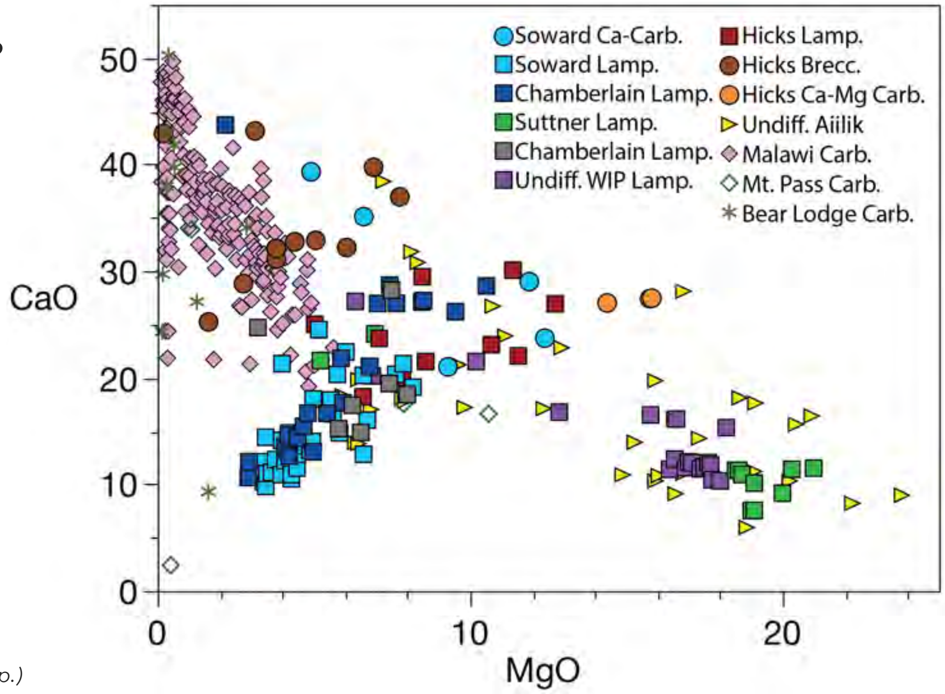
Hicks Dome LLC (Confidential Reports)

Wauboukigou Igneous Province (WIP): igneous affiliated rocks with elevated rare earth element (REE) concentrations and fluorspar associations. These rocks show geochemical similarity to Aillik Bay (Labrador) lamprophyres and carbonatites. Major phases include forsterite, melilite (alnöite), phlogopite, monticellite, Ti-andradite, schorlomite, diopside, nepheline (damtjernite), perovskite, Cr-Ti- spinels, carbonates (aillikite). Lewis and Mitchell, 1987 Wauboukigou Alnöite Province.



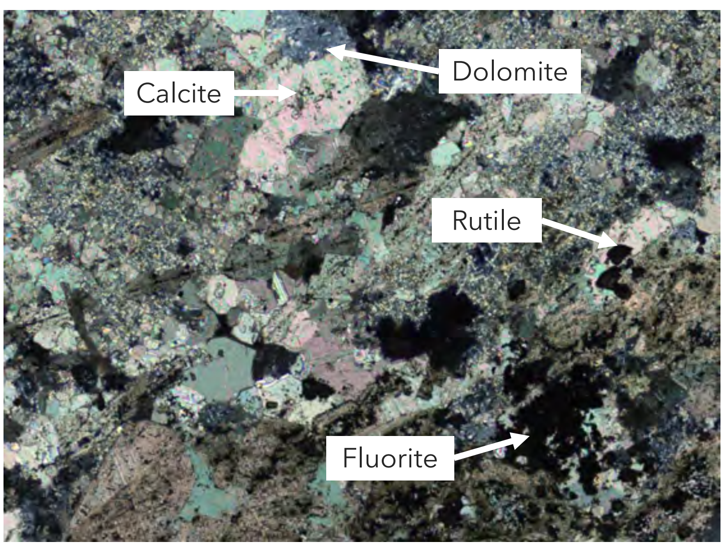
Permian rocks in Illinois show strong similarity to Aillik Bay (Labrador) damtjernites, aillikites, and carbonatites with respect to major and trace element patterns. Five distinct groups can be inferred based on major and trace element patterns.

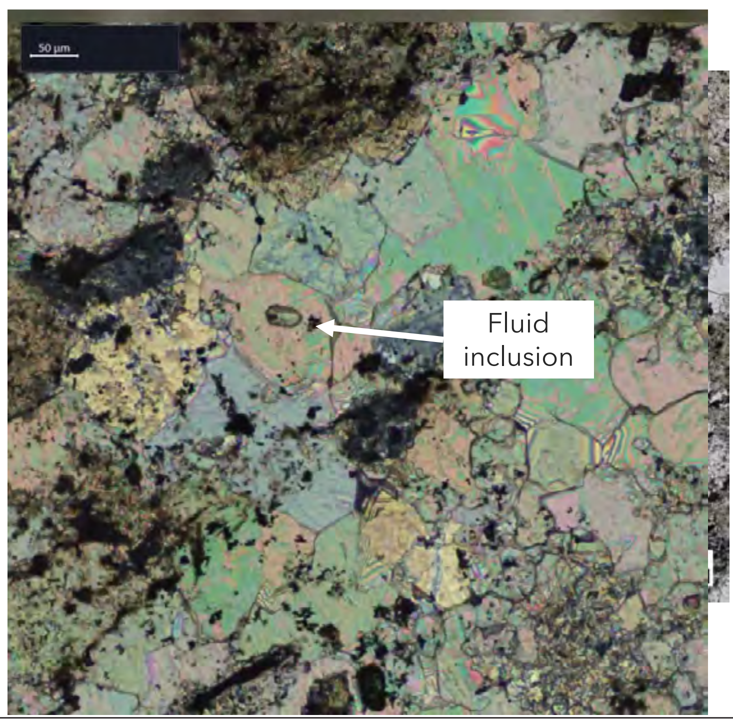
Petrogenesis?



Trela et al., 2022 (In prep.)

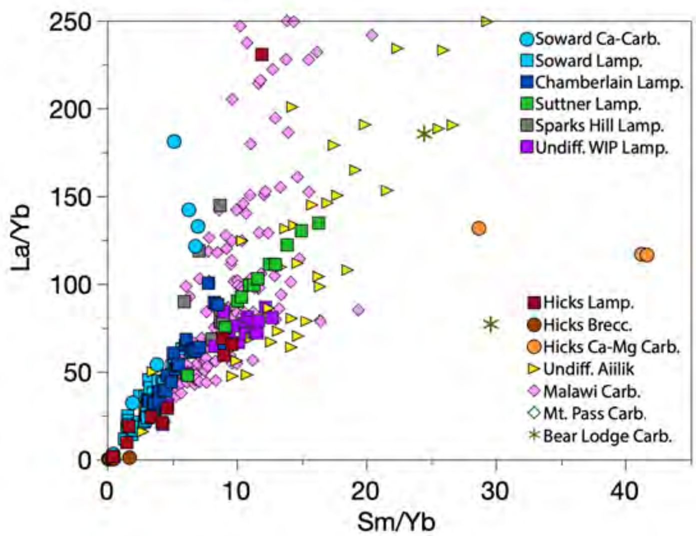
Petrographic analysis shows that Soward samples contain greater than 50% by volume calcite and dolomite. Fluorite is also present in the carbonatite samples.

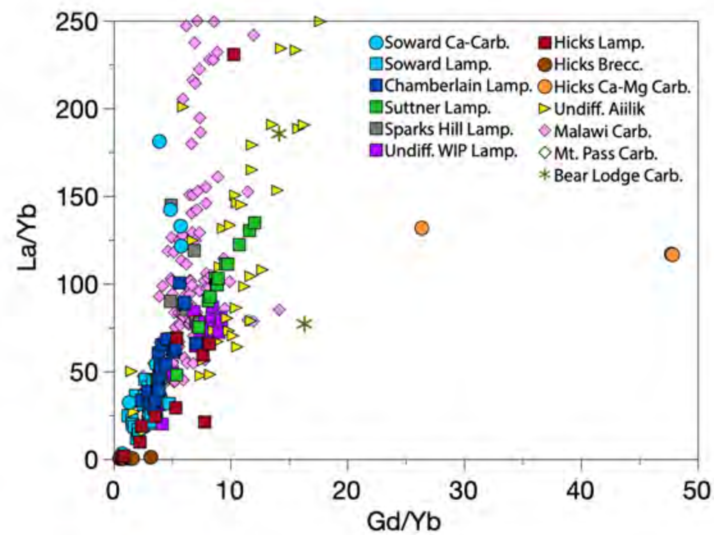




Trela et al., 2022 (In prep.)

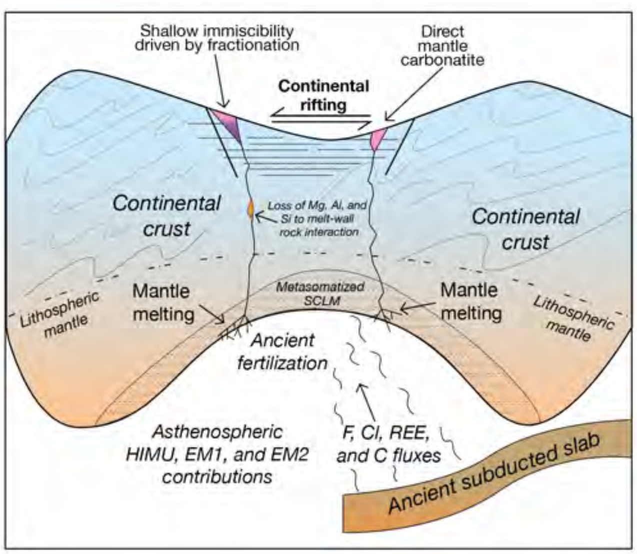
Suttner samples show steepest HREE, possibly representing a higher amount of residual garnet in the source. Low-SiO_2/high CaO carbonatites from Soward (and Hicks Dome) are enriched in LREE with respect to other lamprophyric locations. TREE up to 20,000 ppm at Hicks Dome. 0.9 ~= HREE/TREE



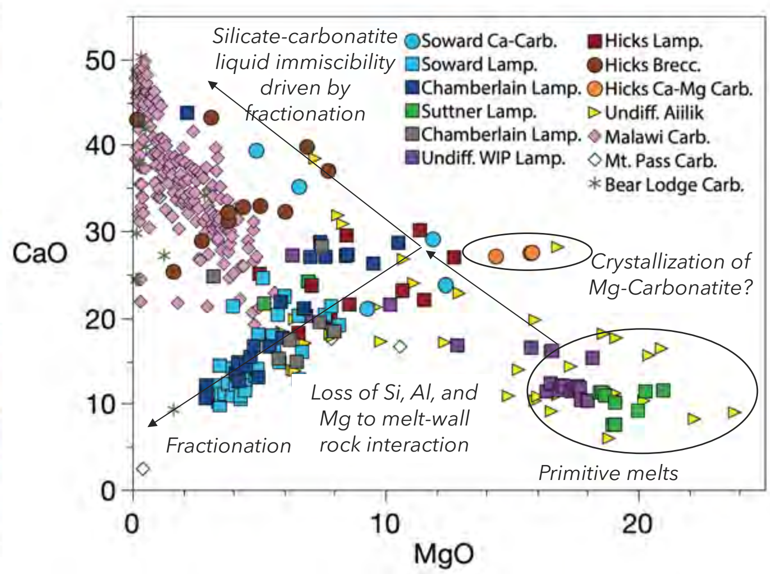


Trela et al., 2022 (In prep.)

Low-degree alkali silicate to carbonatitic, fluid-rich melts from upwelling asthenosphere metasomatized the base of the lithosphere during the rifting of Rodinia (Maria et al., 2019). Decompression melting occurred later at 270 Ma (rifting Pangaea). High-MgO primitive magma reacted with wall rock during ascent. Carbonatite and silicate-melt differentiation driven by fractional crystallization occurred at shallow crustal levels.



Trela et al., 2022 (In prep.)
Modified from Anenburg et al., (2021)



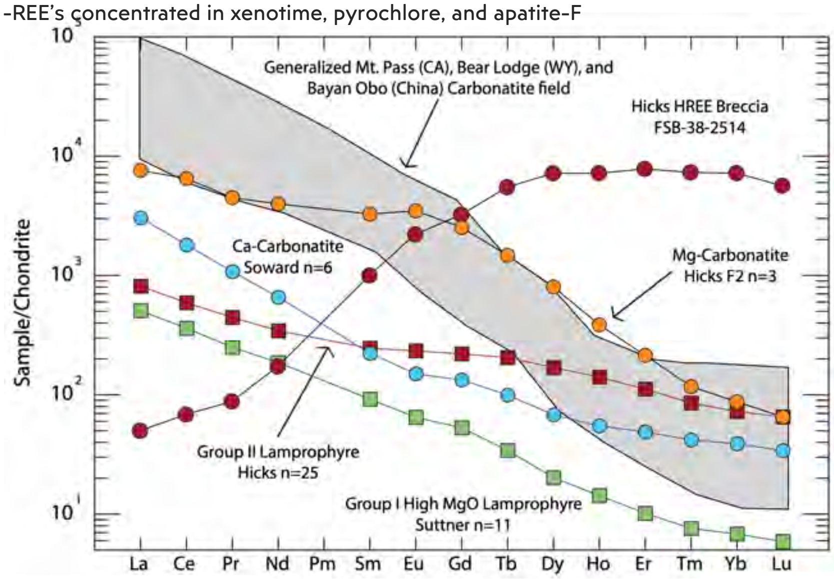
Trela et al., 2022 (In prep.)

HREE enriched mineralized breccias occur at Hicks Dome. REE patterns from Hicks strongly resemble other mineralized breccias from Malawi, Namibia, and Bear Lodge (WY)

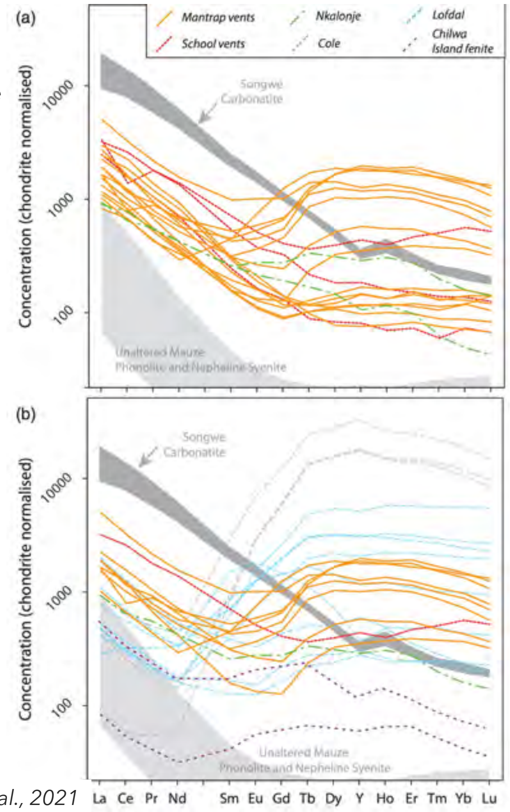
-Carbonatite-derived “brine-melts” break down early crystallizing apatite and REE carbonate minerals.

-Transport HREE through highly permeable breccia pipes. Na/K complexes.

-REE’s concentrated in xenotime, pyrochlore, and apatite-F



Trela et al., 2022 (In prep.)

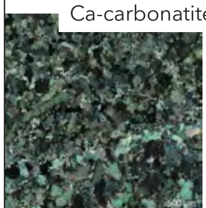


Broom-Fendley et al., 2021

Five distinct groups in the WIP can be distinguished based on major and trace element patterns:

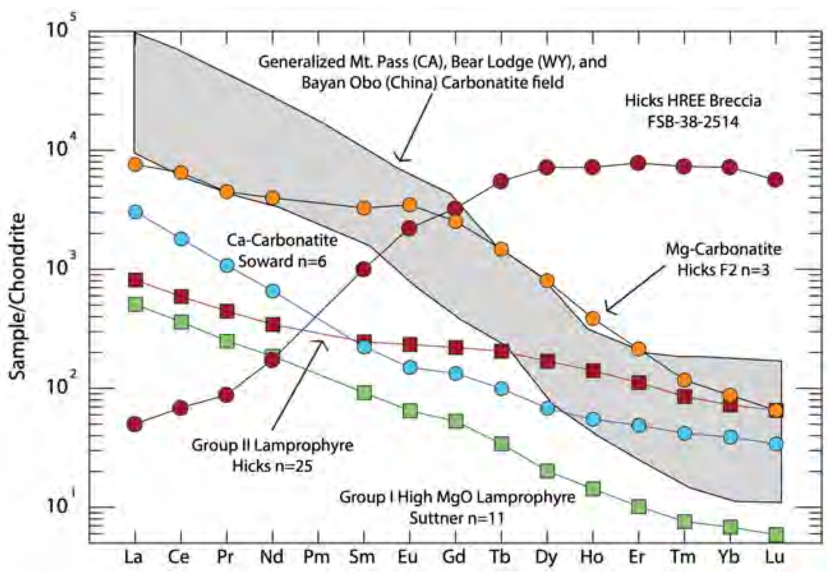
-Group I: High-MgO lamprophyres
-Group II: Low-MgO lamprophyres
-Ca-Carbonatite
-Mg-Carbonatite
-Mineralized Breccia

Ca-carbonatite



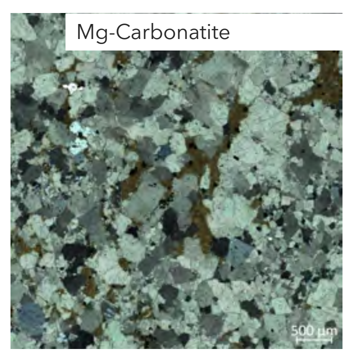
Group II: Low-MgO lamprophyre

Group I: High-MgO lamprophyre



Mineralized Breccia

Mg-Carbonatite



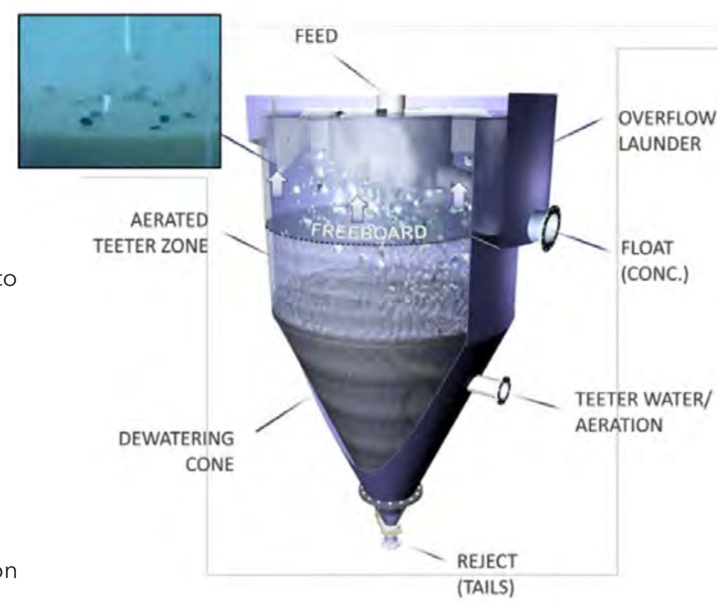
Trela et al., 2022 (In prep.)

REE budget comparison of three major REE prospects in the USA

REE	LREE						HREE												
Location Description	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Sc**	**Y**	**TREE+Sc+Y (ppm)**	**HREE/TREE**
Hicks Dome-HREE Breccia	3	13	4	52	110	91	436	123	966	192	559	77	494	59	414	5,790	9,384	0.97
Hicks Dome-HREE Breccia	14	48	9	79	120	81	411	103	756	145	390	49	280	32	59	4,470	7,045	0.95
Hicks Dome-HREE Breccia	12	42	8	80	148	124	639	197	1,750	389	1,240	179	1,150	138	615	13,400	20,111	0.98
Hicks Dome-HREE Breccia	16	59	11	79	97	76	394	114	942	197	594	83	515	62	316	6,520	10,074	0.97
Hicks Dome-LREE Carbonatite	988	2,410	262	1,180	354	164	407	42	146	15	23	2	9	1	22	351	6,375	0.16
Hicks Dome-LREE Carbonatite	1,050	2,620	273	1,240	371	170	430	44	153	16	24	2	9	1	22	375	6,800	0.16
Hicks Dome-LREE Carbonatite	3,300	6,800	703	3,000	720	249	663	73	292	33	57	5	25	3	104	768	16,794	0.12
Bear Lodge-Carbonatite	10,335	18,713	1,850	7,779	1,286	291	681	55	171	13	20	2	16	2	4	413	41,629	0.03
Bear Lodge-Carbonatite	12,399	23,254	2,297	8,384	1,100	218	534	33	90	6	14	2	19	2	3	249	48,605	0.02
Bear Lodge-Carbonatite	26,285	35,615	2,894		1,499	330	820	46	103	1	0	1	9	1	5	153	67,762	0.02
Bear Lodge-Carbonatite	24,218	41,447	3,955		1,743	331	660	45	124	5	10	2	19	2	4	269	72,833	0.02
Bear Lodge-Carbonatite	10,369	19,118	1,716	5,222	466	81	191	12	37	2	7	1	9	1	3	110	37,345	0.01
Bear Lodge-Carbonatite	10,297	19,889	1,988	7,865	1,006	208	496	31	92	7	17	3	22	3	5	273	42,202	0.02
Mt. Pass-Carbonatite	12,100	17,100	1,420	3,970	280	45	83	9	31	5	9	1	5	1	11		35,070	0.00
Mt. Pass-Carbonatite	18,900	27,300	2,300	6,500	430	62	104	9	20	2	4	0	2	0	7		55,641	0.00
Mt. Pass-Carbonatite	28,800	44,100	4,010	10,900	670	103	154	14	29	5	12	2	14	2	13		88,827	0.00
Mt. Pass-Carbonatite	28,700	41,400	3,810	10,800	830	148	281	25	68	9	13	1	5	1	6		86,097	0.00
Mt. Pass-Carbonatite	28,200	42,000	3,790	10,200	640	147	158	14	27	3	6	1	3	0	6		85,195	0.00

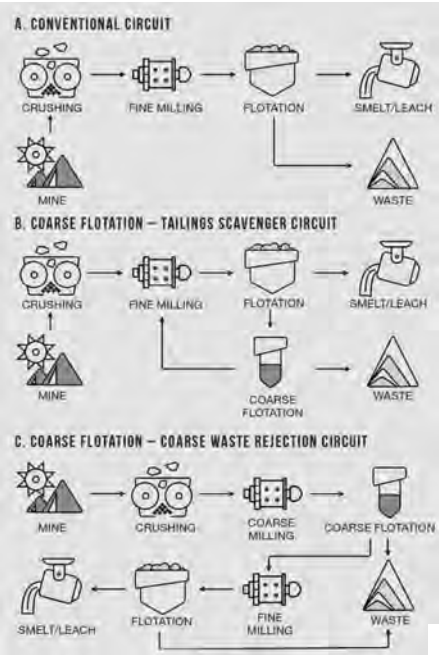
Collaborative work with Dr. Rick Honaker (University of Kentucky). Hydro-floatation technology and the application to Hicks Dome critical mineral separation. Eriez' *HydroFloat*™ technology. (US Patent No 6,425, 485, 30 July 2002)

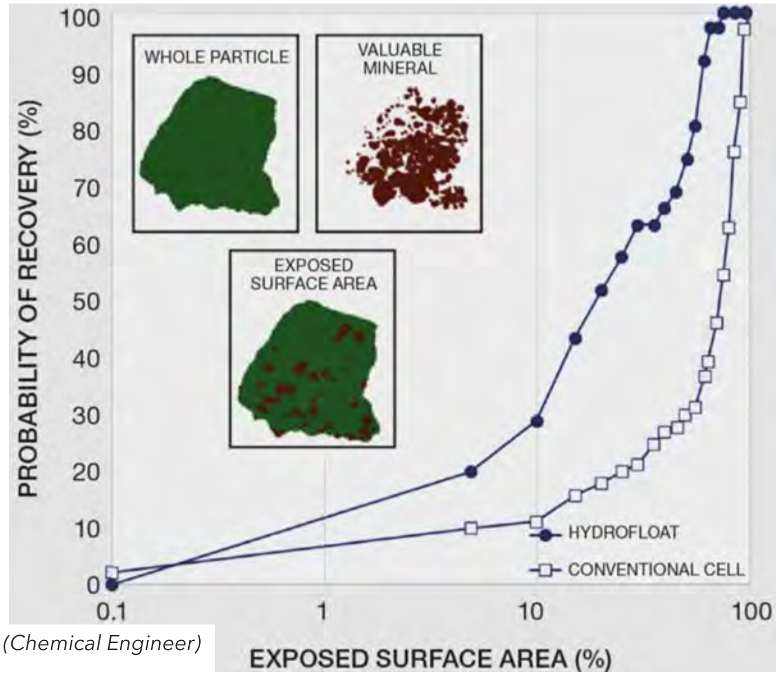
- The *HydroFloat* cell works on combining the principals of flotation with hindered settling.
- Key characteristic of the *HydroFloat* cell is the aerated fluidized bed.
- The fluidization water, air and frother is injected through a cavitation tube to generate fine bubbles and then conveyed into a distribution manifold.
- Fine bubbles introduced directly into fluidized bed enhances probability of bubble-particle collisions.
- Bubble attachment reduces the relative density of the resulting bubble-particle aggregates allowing them to be separated out of the fluidized bed.
- Mineralized particles either float immediately or are collected on the teeter-bed surface until sufficient bubbles accumulate to assist with hydraulic transfer to the overflow launder for collection as concentrate.



Vollert et al., 2018

Benefits of the *HydroFloat* technology include ~50% reduction in energy, enhanced recovery (including coarser fractions), and recyclability. Demonstrated to recover coarse potash, phosphate, coal, vermiculite, spodumene and diamonds.



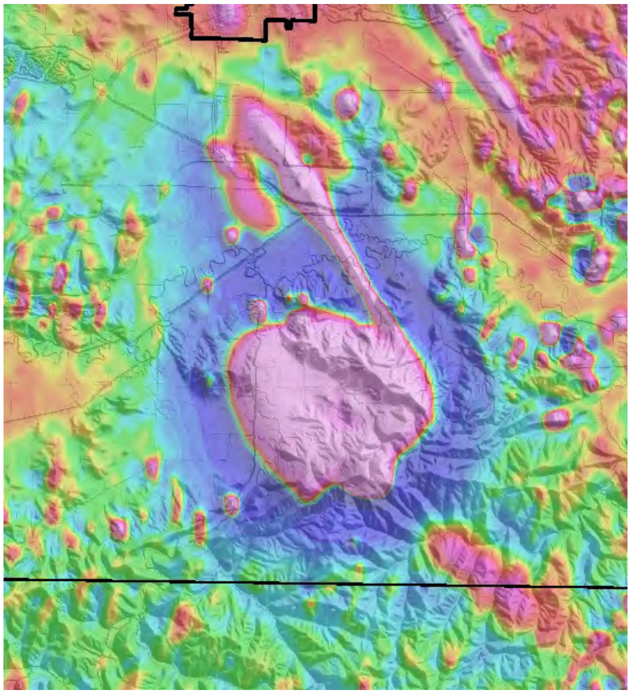


Forbes et al., 2021 (Chemical Engineer)

Future Work:

- Sr-Nd-Pb radiogenic isotopes. Mantle source(s) for lamprophyres, carbonatites, and mineralized lamprophyric breccias?
- Fluid inclusion work. Constrain P-T-X conditions of fluids.
- High-precision trace element laser work. Fluorite, Xenotime, and phosphates.
- Earth-MRI 2022-2024 budget: regolith/soil sampling, fenite mapping, stream sampling, XRF mapping.
- DARPA proposal
- DoE collaboration
- Experimental petrology
- **Drill Hicks Dome deeper. Larger sample size for future metallurgical work.**

Carrier Mills Anomaly

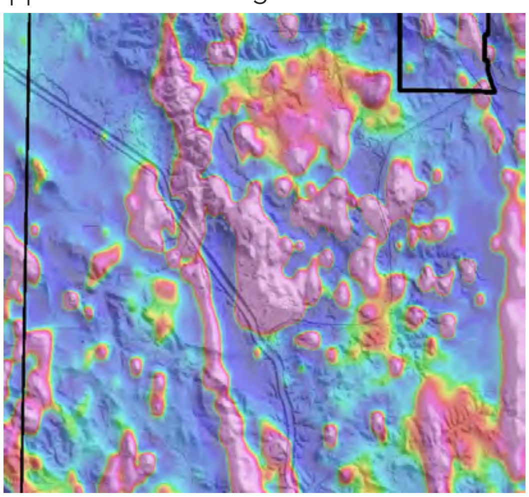


This musical note of an anomaly is mapped south of Carrier Mills, Illinois. The anomaly has a distinct magnetic core surrounded by a non-magnetic zone. Signatures like these could be interpreted as an intrusive center surrounded by hydrothermally altered rock where hot fluids have demagnetized or lowered the magnetic susceptibility of the surrounding rocks.

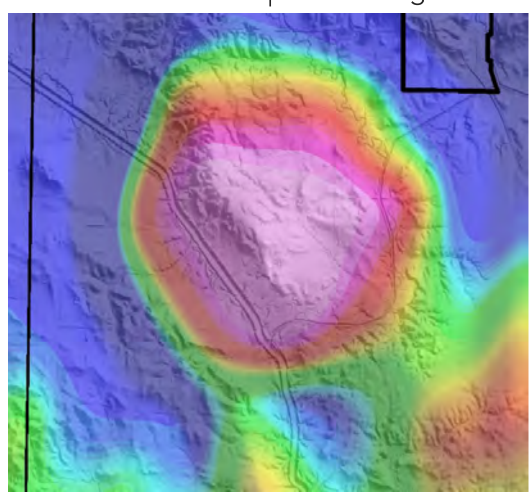
It would be interesting to see if the low around Carrier Mills and the magnetic low surrounding the Coefield anomaly (and several other similar anomalies identified in the new survey) might exhibit geochemical signatures indicative of alteration and metal concentrations.

Additionally, if this presumed alteration has affected rocks in the very shallow crust, there might be a radiometric signature at the surface. We'll be able to assess that once the preliminary radiometric data are available. Hicks Dome, for example, has a radiometric signature.

Omaha Dome, Illinois
Upper 140 m RTP mag on terrain



Omaha Dome, Illinois
140 m to 1000 m depth RTP mag on terrain

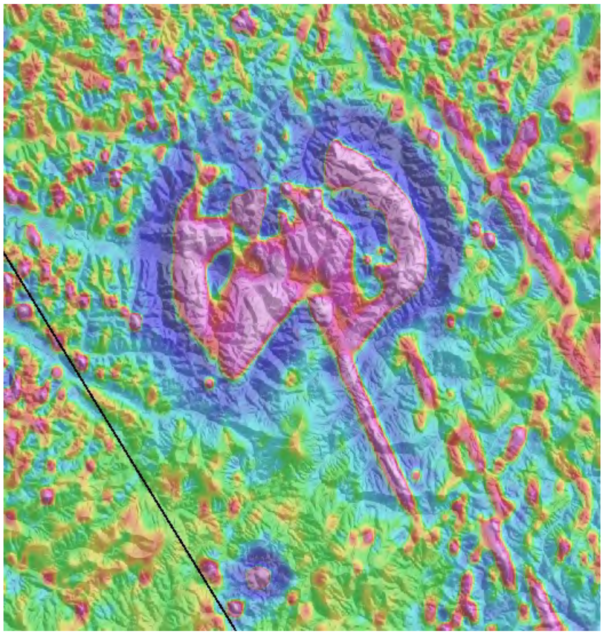


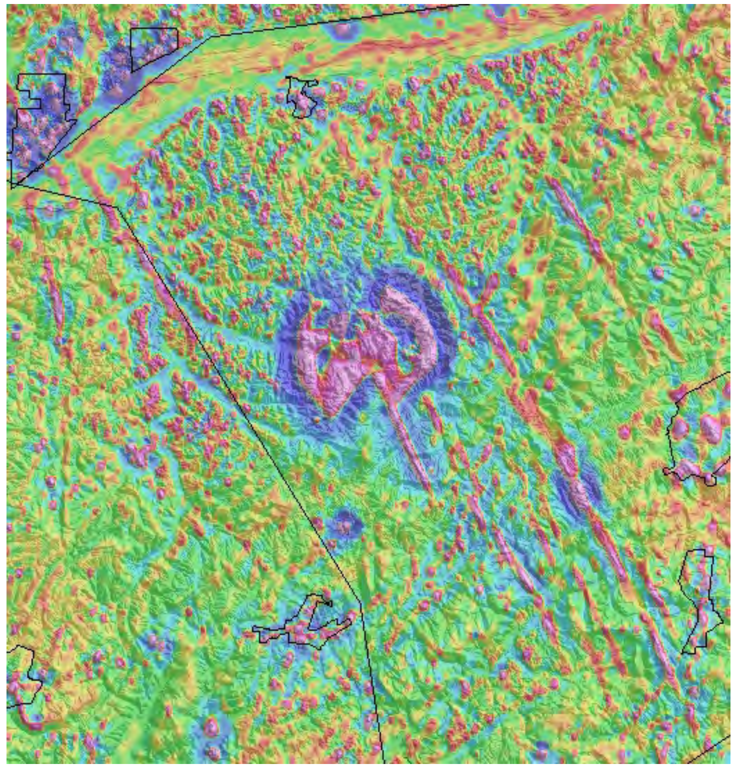
Lots of dikes are evident in the shallow (< 140 m depth) layer magnetic map and will be useful to refine the geology. Elongate magnetic anomaly highs are present throughout the survey and can be used to extend the mapping of known ultramafic dikes and as yet unmapped dikes.

These two maps are from the same area around the Omaha Dome. The Dome can be best seen on the map on the right which shows a circular magnetic source, deeper than 140 m, underlies and is the source for (?) the dikes and scattered mag sources within the upper 140 m.

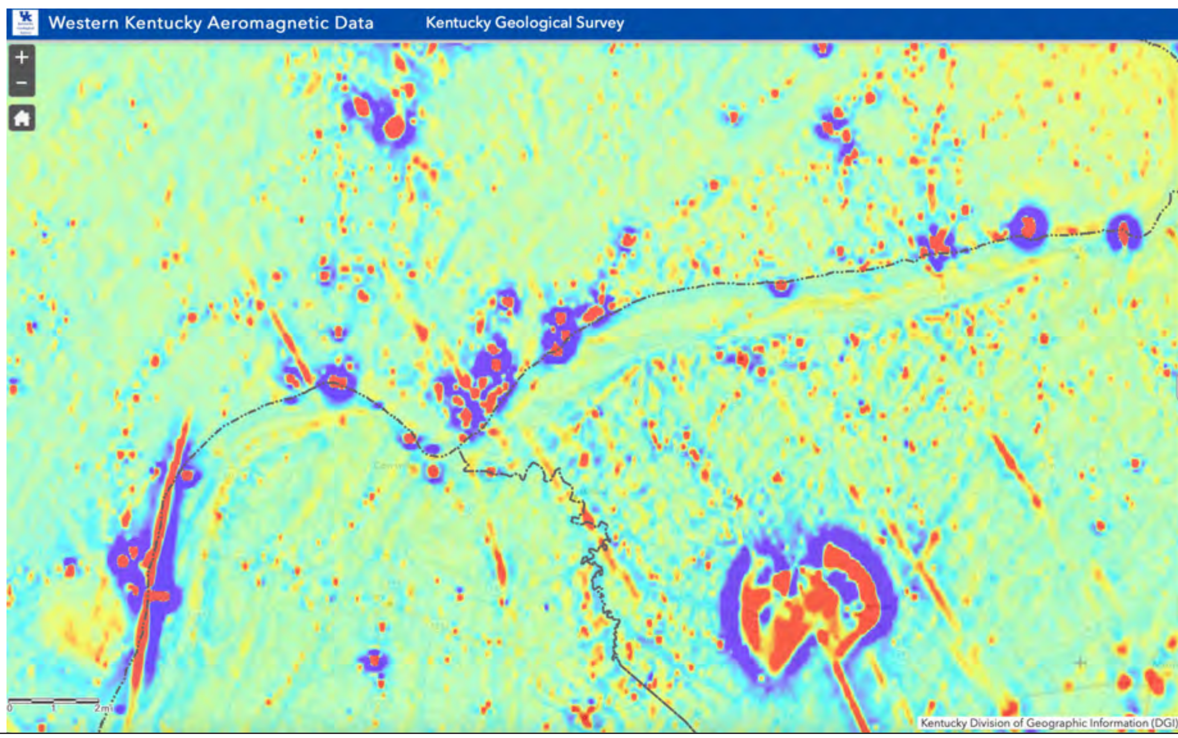
Coefield Anomaly, Kentucky

Upper 140 m RTP magnetic anomaly on terrain
Numerous dikes confirmed by KGS field mapping





Partial map of aeromagnetic survey. Northern extent ends at Hicks Dome. Southern extent shows the Coefield (a.k.a. Lollipop anomaly) in Kentucky.



Many thanks to everyone involved with this project:

- Jared, Mingyue, Kelly, Kristina, Scott, Pat, Dick, and Craig at the ISGS/University of Illinois
- Laurence Nuelle at Hicks Dome LLC for opening sample collection to ISGS
- Esteban Gazel at Cornell University for pointing me in all kinds of directions for data and ideas
- Anne McCafferty at USGS for geomagnetic modeling and discussions
- Gina Lukoczki at the Kentucky Geological Survey
- Larry Nuelle at Hicks Dome LLC for opening core repository to ISGS
- Craig Dietsch at University of Cincinnati for numerous discussions
- Tony Maria at University of Southern Indiana for lively discussions
- Brett Denny, my predecessor at the ISGS for providing me with lots of data, maps, and papers
- Max Molinarolo Ben Clement Museum (KY) for assisting me in the field
- Madi and Ada for all their support. Also Matt, Erica, and Jake!

Thank you!