Energy & Environmental Research Center (EERC)

SAMPLING, CHARACTERIZATION, and ROUND-ROBIN ANALYSES OF DOMESTIC U.S. COAL-BASED RESOURCES CONTAINING HIGH RARE-EARTH ELEMENT (HREE) CONCENTRATIONS

DOE CONTRACT DE-FE0029007

DOE NETL Annual Project Review Meeting, April 9–11, 2019

Crosscutting, Rare-Earth Elements, Gasification Systems, and Transformative Power Generation

Chris J. Zygarlicke

April 10, 2019 Session C7: Process Economics & Embedded REE Demand

PROJECT DESCRIPTION

- **DOE NETL:** Vito Cedro and Mary Anne Alvin
- **Strategic alignment with DOE:** efficient rare-earth element (REE) resourcing and cost-competitive domestic supply, recovery, coal by-product utilization
- **Team**
  - University of North Dakota (UND) Energy & Environmental Research Center (EERC); UND Institute for Energy Studies (IES)
  - University of Kentucky (UK) Center for Applied Energy Research, the Kentucky Geological Survey (KGS) under the University of Kentucky Research Foundation, and Microbeam Technologies Inc. (MTI)
  - North Dakota Geological Survey (NDGS)
- **Partners:** Several U.S. coal mining companies and utilities
- **Contract:** October 2017 – September 2019

North Dakota Geological Survey 1895

Kentucky Geological Survey

National Energy Technology Laboratory

ACKNOWLEDGEMENT

- Kentucky Geological Survey (KGS)
- North Dakota Geological Survey (NDGS)
- Mining Companies
  - North American Coal Company
  - Kiewit Mining Group
  - Westmoreland Coal Company
  - BNI Coal Company
  - Leonardite Products LLC
  - Alliance Coal Company
  - Blaschak Coal Company

PROJECT OBJECTIVES

- Determine sources of coal and coal-related materials >= 300 parts per million (ppm) REEs as removed from the ground.
- Identify/review sample collection, preparation, and handling methods and acquire samples.
- Conduct advanced characterization on sample subsets for better understanding of modes of occurrence.
- Perform a round-robin interlaboratory study (RRIS) to determine the lab-to-lab and method-to-method variability in the REEs.
- Provide DOE NETL data for upload to NETL EDX.

PROJECT SAMPLING LOCATIONS

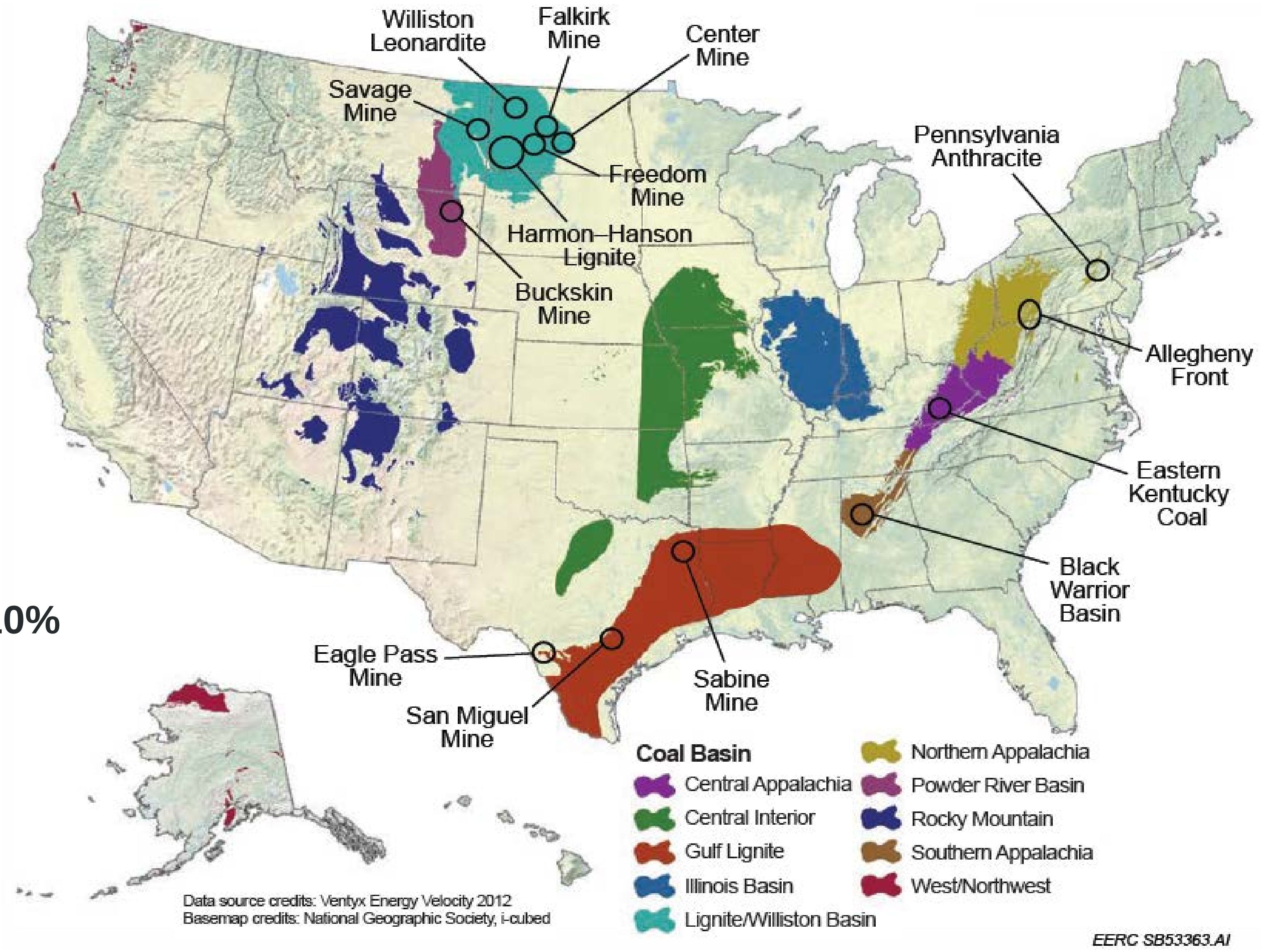
Coal Sources and Samples

Western Coal and North Dakota Lignite Emphasis

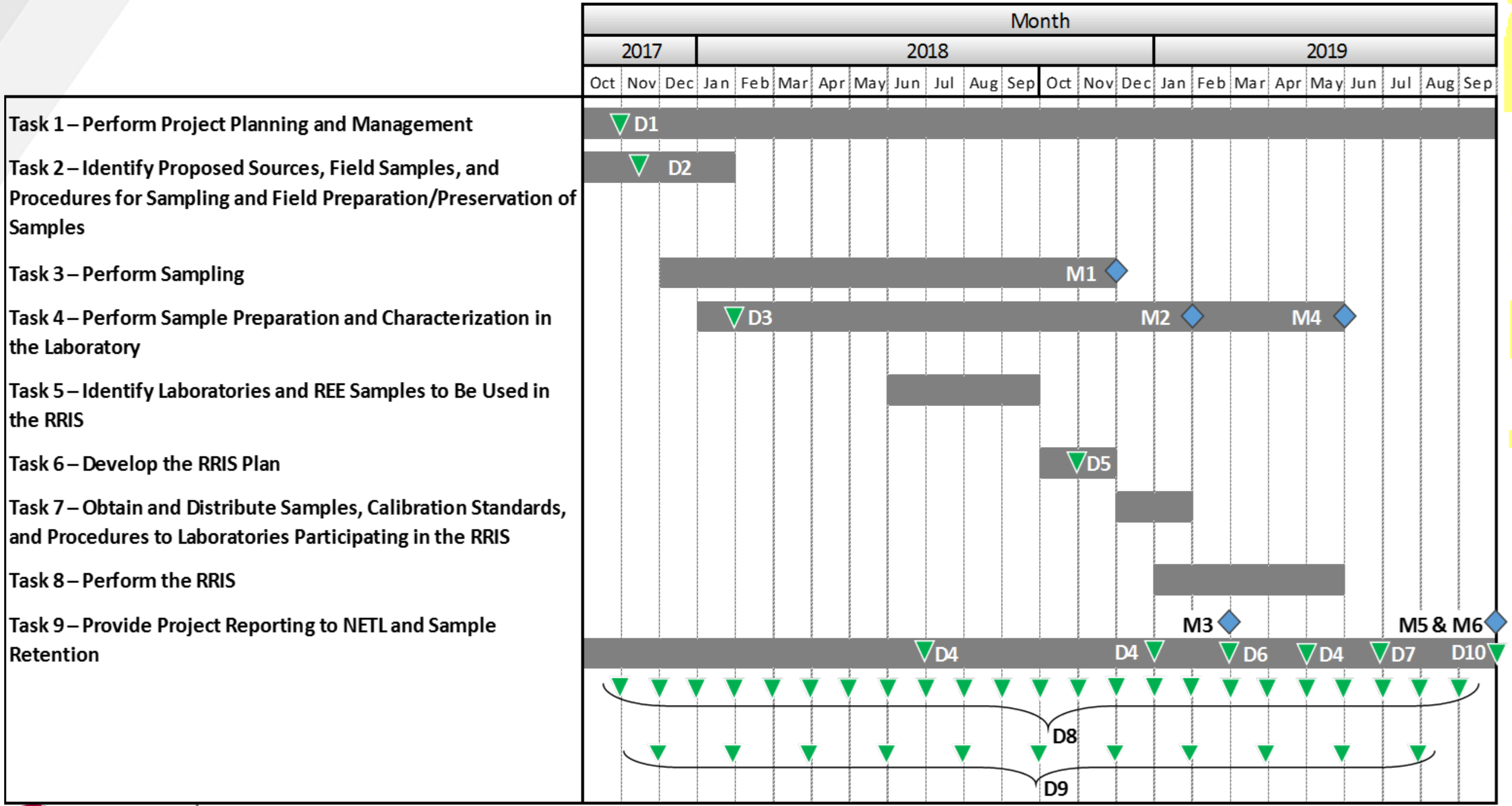
80%

10%

10%



PROJECT UPDATE



D1	Updated Project Management Plan
D2	Final Sampling Plan
D3	Final Sample Preparation and Characterization Plan
D4	Sampling and Characterization Information
D5	Final RRIS Plan
D6	Interim Report – Sampling and First-Pass Characterization Across All Bulk Parent Materials
D7	Laboratory Analyses and Statistical Analysis Data
D8	Technical Progress Reports
D9	Technical Status Updates by Phone
D10	Final Report
M1	Complete Field Sampling
M2	Complete Sample Preparation and Characterization of All Bulk Parent Materials
M3	Complete Interim Report Based on Sampling and First-Pass Characterization Across All Bulk Parent Materials
M4	Complete Sample Preparation and Characterization of All Materials
M5	Complete Final Project Report
M6	Complete Sample Preservation for Retention (storage)

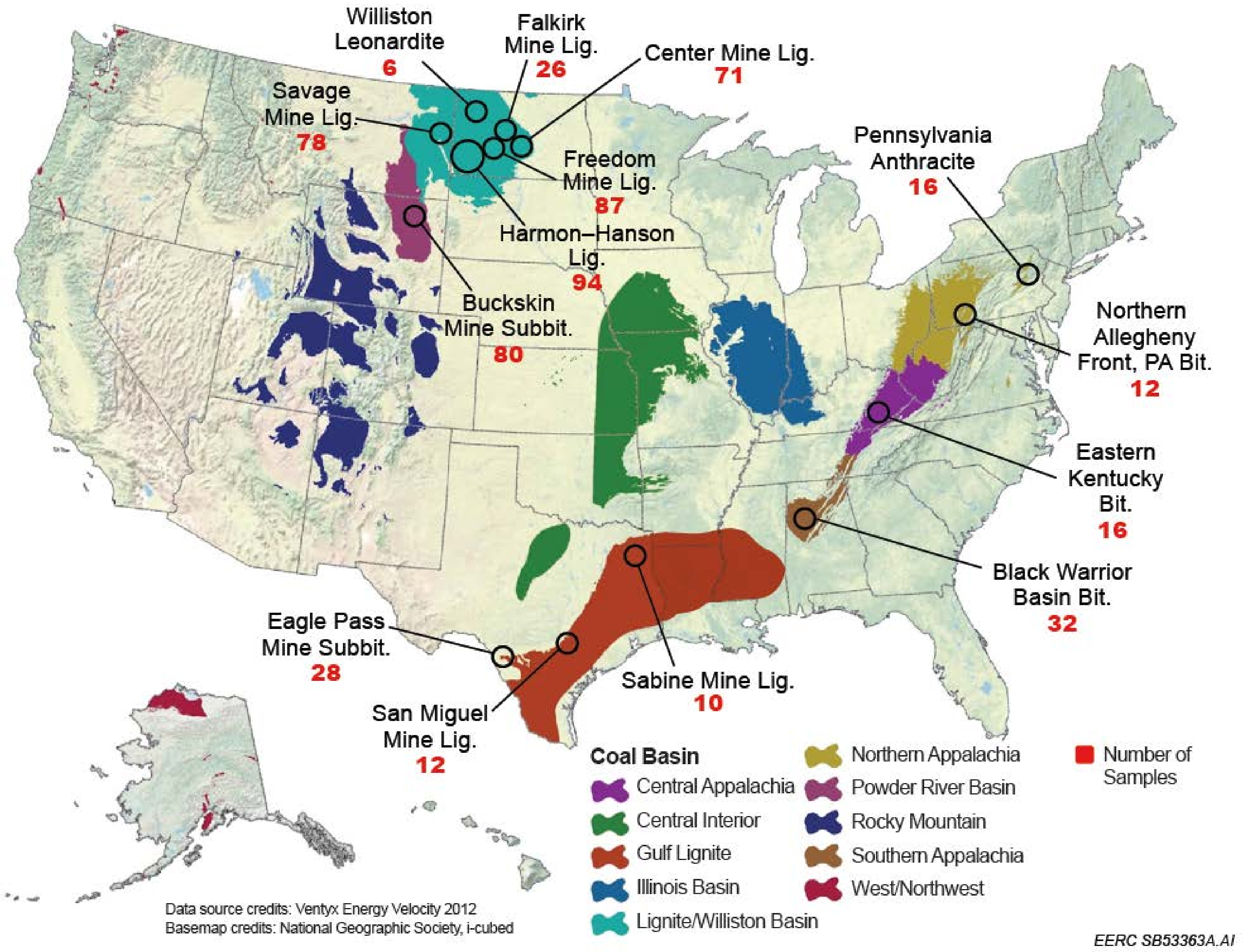
STANDARD AND ADVANCED METHODS

- Methods
  - ASTM: preparation, P/U, and moisture, ash, and REE contents.
  - REEs:
    - ♦ UND digesting and analysis using ASTM Method D4503 including inductively coupled plasma–mass spectrometry (ICP–MS)
    - ♦ UK-CAER ASTM D6357-11 using a combination of ICP–MS and ICP–OES (optical emission spectroscopy)
- Advanced characterization to aid in mode of occurrence evaluation:
  - FESEM, TEM, chemical fractionation characterization of REE-rich particles
  - New CCSEM method for REEs
  - Gravity separation for separating and concentrating REE-rich fractions

PROJECT RESULTS – SAMPLE COLLECTION

- Acquired coal and coal-related samples nonexistent, underrepresented, or having incomplete information in current databases.
- Contracted for 582 samples, collected over 600 representing 12 unique locations that span six major coal basins.
- UND and NDGS sampled western coal basins.
- UK-CAER and KGS sampled eastern U.S. coal basins.
- Non-coal: fly ash, bottom ash, acid mine drainage, clay-shale partings, and roof rock.

Sampling Effort



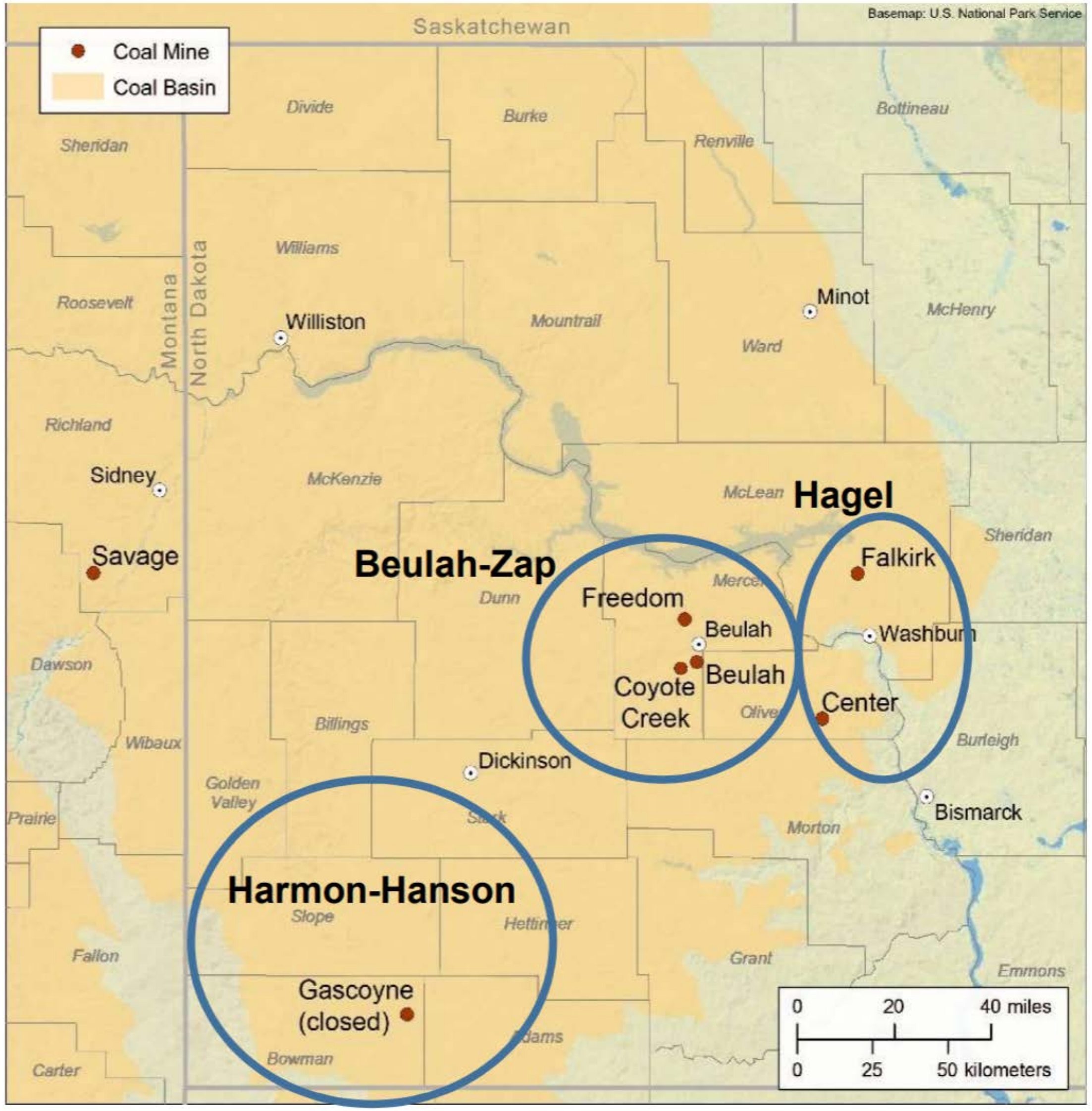
FINAL SAMPLE TOTALS AND TREEs

- Samples
  - 648 samples
    - ♦ 560 from western resources
    - ♦ 88 from eastern resources
    - ♦ 46 samples are ash/AMD
- TREEs >= 300 ppm dry **ash** basis
  - 240 coal samples
  - 259 coal-ash samples
- TREEs >= 300 ppm dry **mass** basis
  - 21 coal samples
  - NOTE: 97 samples had levels >200 ppm

Outcrops in southwestern North Dakota, 2018

FORT UNION GROUP–WILLISTON BASIN FOCUS

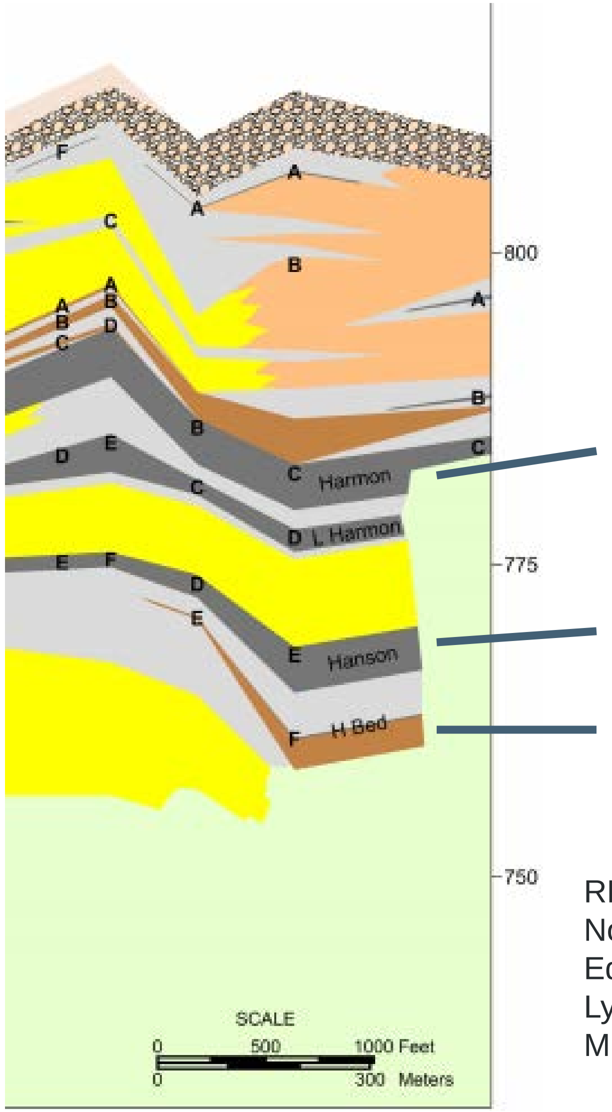
- 25–30 B tons lignite recoverable from world's largest lignite deposit 350 B tons
- ~30 M tons/yr lignite used; 800-year supply
- Mature coal utilization infrastructure, top 10 coal producer, supplies 66% of ND electricity, Project Tundra FEED study for commercial CO_2 capture.
- 3 major coal zones; Beulah-Zap, Hagel, Harmon-Hanson (mining of this lignite ceased in 1995)
- 7 lignite-fired power plants > 4000 MWe total capacity.



Critical Challenges. Practical Solutions.

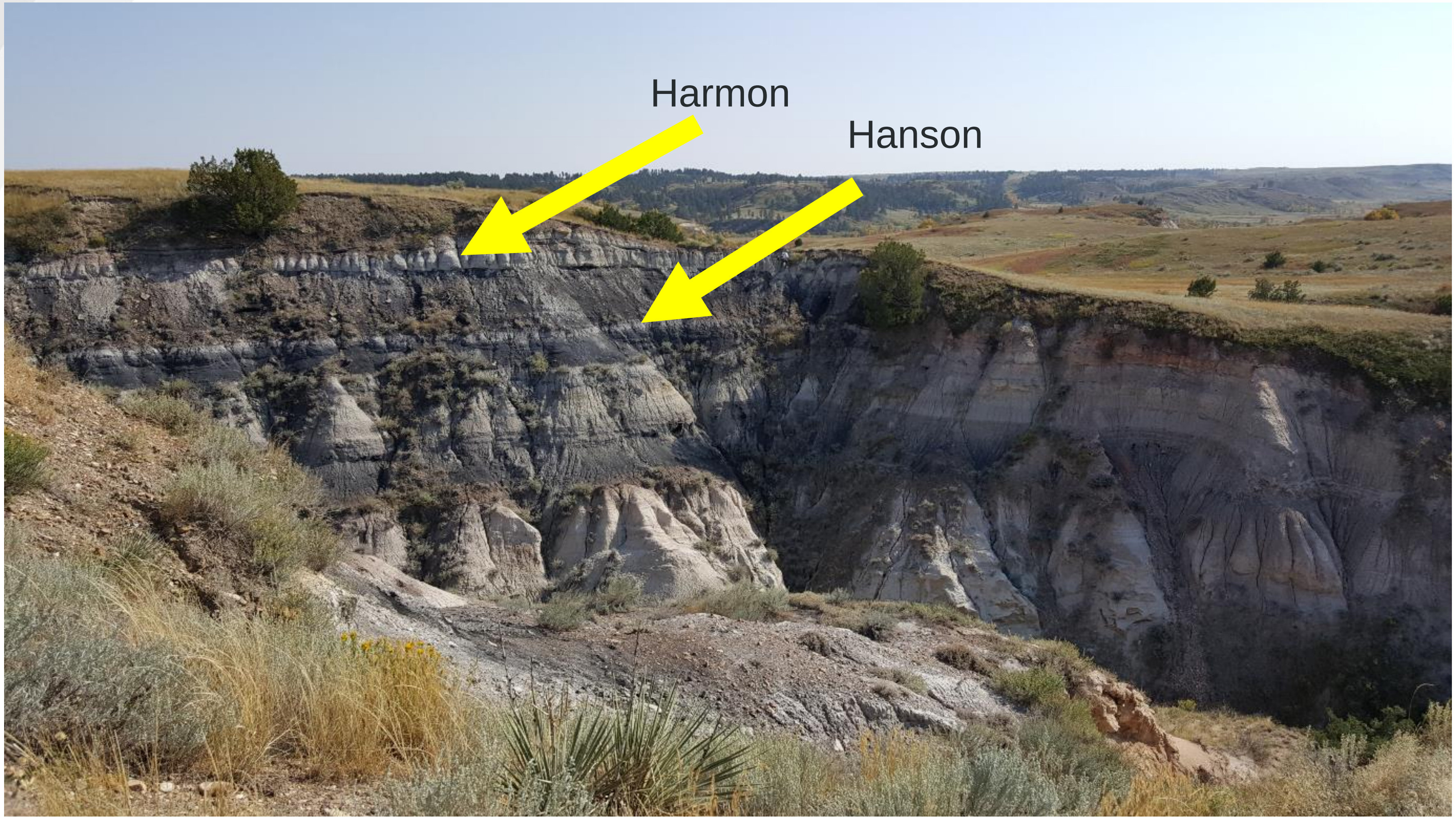
HARMON–HANSON LIGNITE POTENTIAL

- Outcrops of the Harmon, Hanson, and H bed seams, Fort Union Group, in SW North Dakota
- 6–20' accessible seams, former mining operations
- 144 samples collected
- Upper seams show markedly higher TREEs; Harmon–Hanson ~400 ppm and H Bed >1000 ppm dry coal basis.



REPORT OF INVESTIGATION NO. 119
North Dakota Geological Survey
Edward C. Murphy, State Geologist
Lynn D. Helms, Director Dept. of Mineral Resources, 2018, p. 13

HARMON–HANSON SAMPLING LOCATION



Harmon–Hanson lignite at top of outcrop

Thin 16-inch H-Bed does not occur here

FREEDOM MINE – BEULAH–ZAP LIGNITE

- Active stable mine-mouth operations of North American Coal Co. with good potential for lower cost extraction
- Lignite from Twin Buttes and Beulah–Zap seams
- Beulah–Zap 18 to 22’ seams
- Twin Buttes 6’ seams with 25–30’ of overburden where actively mined
- 93 samples were collected.
- Limited >300-ppm samples, but show high HREE/LREE ratio of 0.89

Photo: Star Tribune, AP Photo/James MacPherson

SAVAGE AND CENTER LIGNITES

- Savage (MT) lignite
  - Little existing characterization data
  - All REE levels <200 ppm (mass basis)
  - Indicators of volcanic ash deposits (rhyolitic glass) will be examined in samples near top of seam and near shale partings.
- Center (ND) lignite
  - 71 samples; several with >1 HREE/LREE, but TREEs <40 ppm

Photo: Westmoreland Coal Company

BUCKSKIN MINE – ANDERSON AND CANYON

- Powder River Basin in Wyoming and part of the Fort Union Group.
- The USGS CoalQual database showed several samples >200 TREEs; collected 80 coals and a few power plant ashes.
- Coals ranged from 10- to 210-ppm TREEs, with 17% avg. ash content
- Power plant fly ash/bottom ash samples >300-ppm TREEs

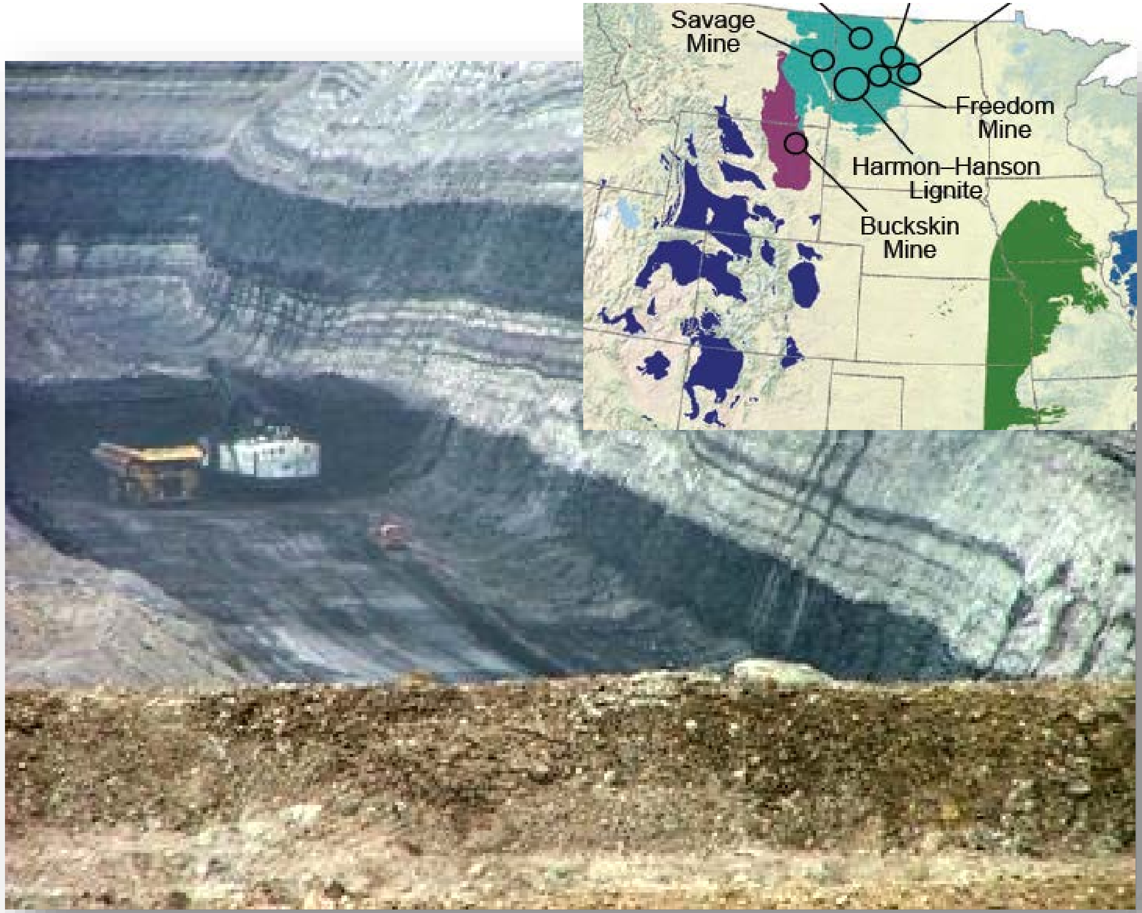


Photo: Wyoming Public Media

TEXAS GULF COAST COAL TARGETS

- Strip-minable ~4-Mtpy thin multiseam coal mines part of the Gulf Coast or Texas Lignite Basin
- San Miguel Mine – Jackson Coal (lignite) extensive mining infrastructure, 12 samples averaging 125-ppm TREEs.
- Sabine Mine – 4 Mtpy, Wilcox lignite, ten samples averaging ~45-ppm TREEs.
- Eagle Pass Mine – Olmos Coal, (subbitum.) and two out of 28 samples had ~350-ppm TREEs dry mass basis.

Photo: William Luther/San Antonio Express-News

SELECT WESTERN SAMPLES >300-PPM TREES, PPM DRY SAMPLE BASIS

Description	Seam	State	Total REEs Y + Sc	HREE/LREE	Ash %
Lignite, Outcrop, Upper Seam	Harmon	ND	439	0.46	28
Lignite, Outcrop, Lower Seam	Harmon	ND	261	0.44	21
Lignite, Outcrop, Top Seam	Hanson	ND	370	0.38	39
Lignite, Outcrop, Top Seam	H bed	ND	1024	0.20	60
Lignite, Outcrop, Lower Seam	H bed	ND	345	0.33	92
Lignite, Freedom Mine	Twin Butte	ND	365	0.89	30
Fly Ash, Subitum., Buckskin Mine	Anderson	WY	403	0.36	NA
Bottom Ash, Subitum., Buckskin Mine	Anderson	WY	343	0.39	NA
Subitum., Buckskin Mine	Anderson	WY	10–210	0.25–0.50	6–75
Eagle Pass (A1 P301C) BU – coal	Olmos	TX	340	0.34	49
Eagle Pass (A1 P301C) B IB middle – coal	Olmos	TX	315	0.26	91

EASTERN U.S. (APPALACHIAN) RESULTS

- 10% of project samples (88) collected from eastern U.S. coal mines and processing plants
  - 12 Pennsylvania bituminous
  - 18 Pennsylvania anthracite – Llewllyn
  - 26 East Kentucky bituminous
  - 32 Alabama bituminous
- 12 ash/AMD samples
- No coal samples >300 ppm TREEs, mass basis
- 69 samples > 300 ppm TREEs ash basis

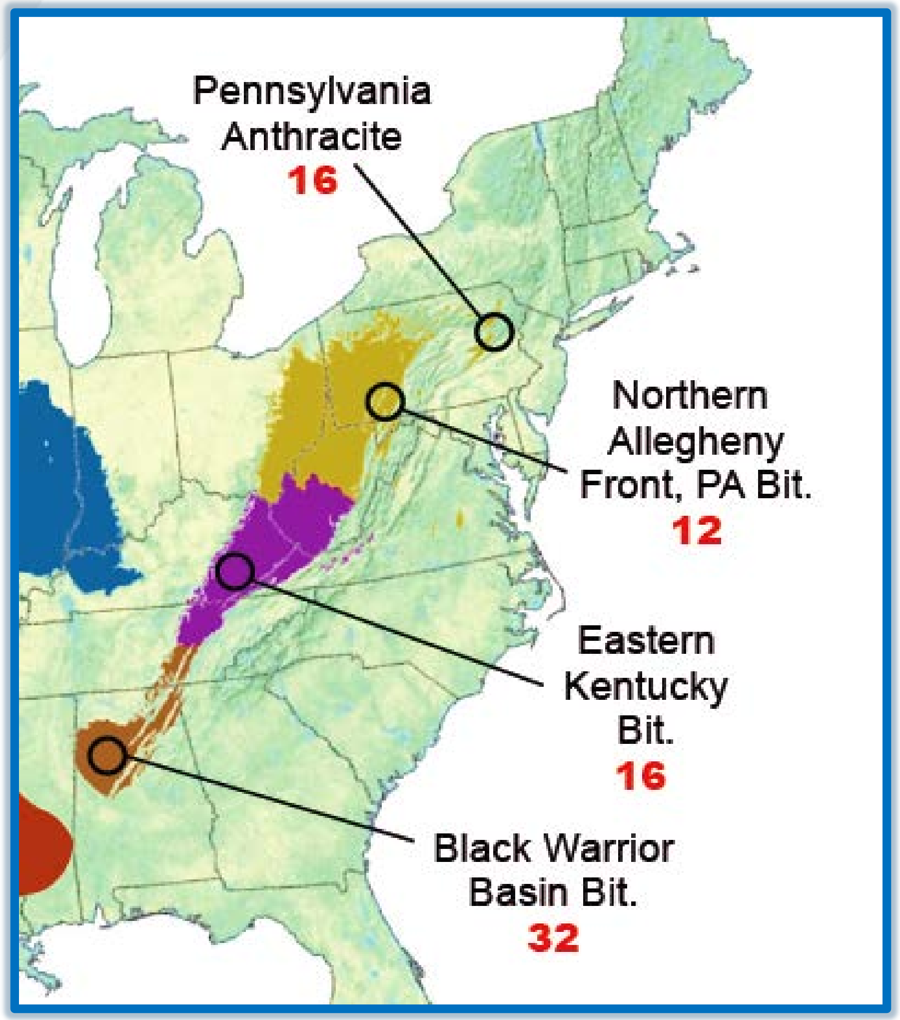
4-AMD (acid mine water, sludge) Central Appalachian Eastern Kentucky

1-AMD (sludge and coal fines) Northern Appalachian, Pennsylvania Anthracite

EASTERN SAMPLES >300-PPM TREES, PPM DRY MASS BASIS

Description	Seam	State	Total REEs Y + Sc	HREE/ LREE	Ash %
Bituminous, Carb. Shale	Pottsville	AL	317	0.24	89
Bituminous, Roof Rock	Pottsville	AL	537	0.29	94
Bituminous, Fly Ash/FGD	Breathitt	KY	326	0.50	86
Bituminous, Bottom Ash	Breathitt	KY	392	0.35	69
Bituminous, Fly Ash	Breathitt	KY	653	0.44	96
Bituminous, Stoker Ash	Breathitt	KY	776	0.37	96

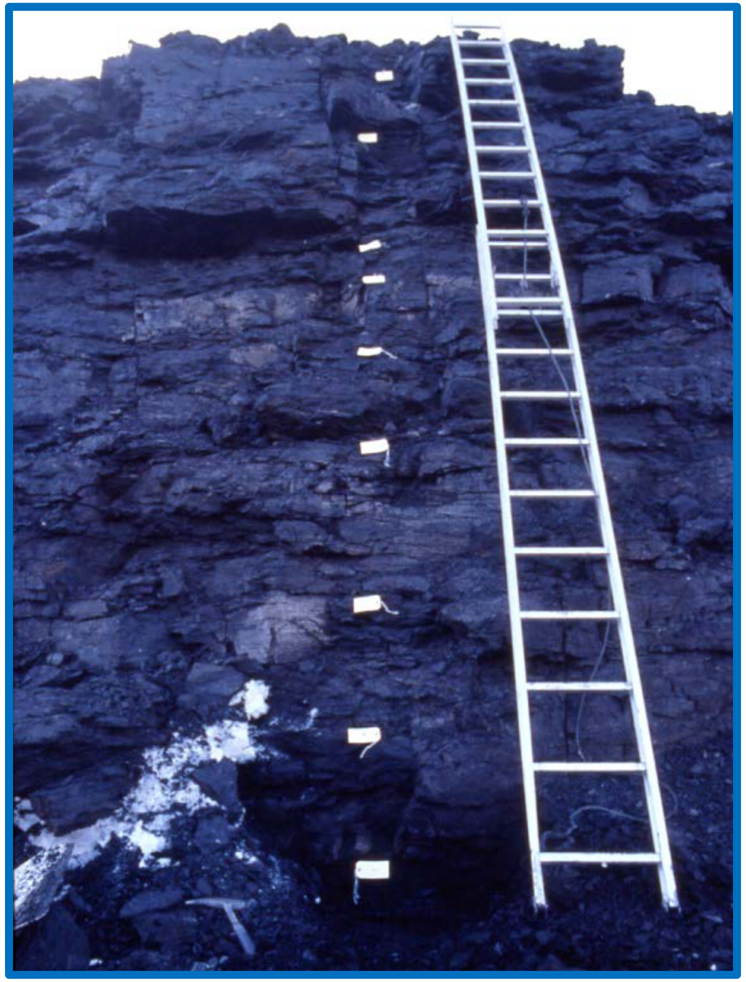
ALABAMA



- Underrepresented southern Appalachian bituminous coal region
- Sampling from southeast edge of Alabama Black Warrior Basin
- Hydrothermal metamorphism with potential for high TREE contents.
- 20/32 coals >300 ppm TREEs on ash basis, highest at ~570 ppm.

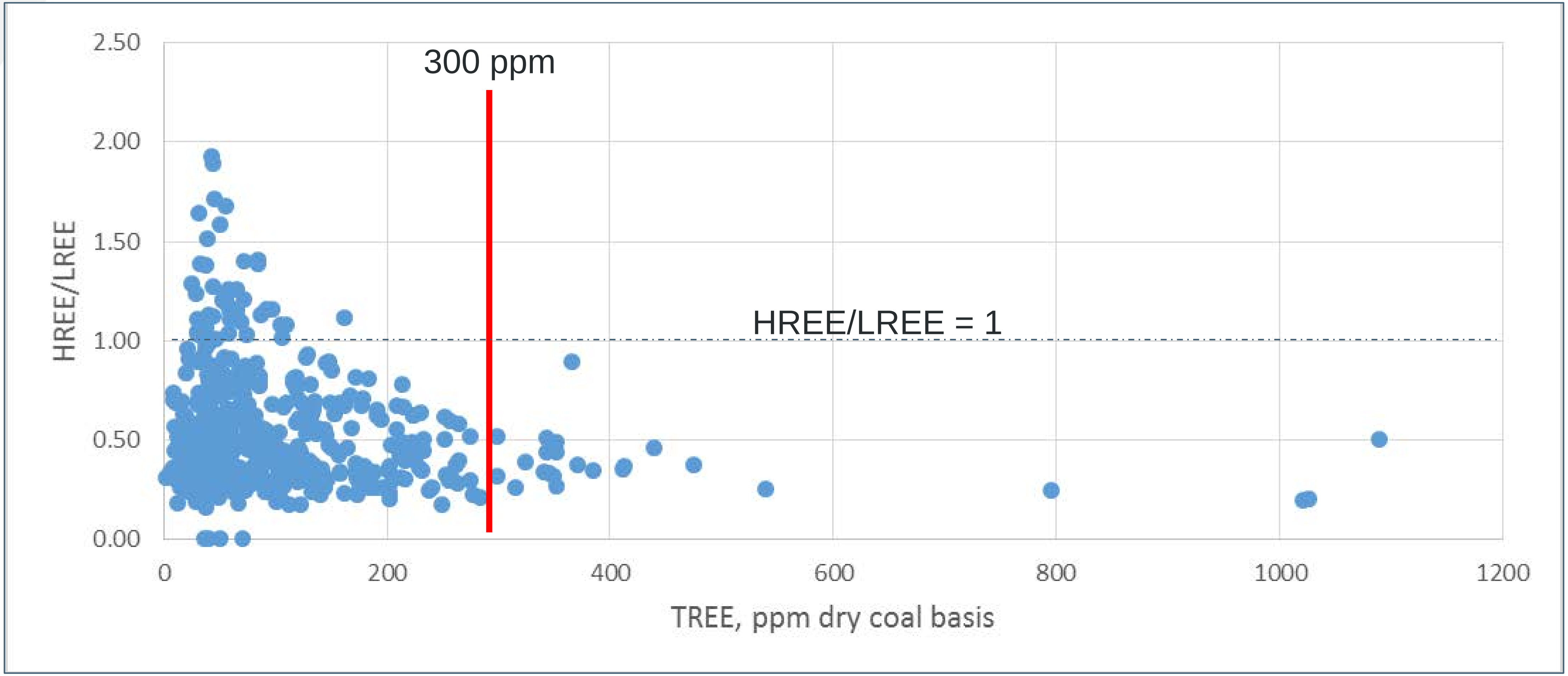
RESULTS – REE TRENDS IN LOW-RANK COALS

- Twofold focus of sampling: 1) maximize samples >300 ppm and 2) learn more about modes of occurrence and trends of distribution for future reserve estimation and extraction methods.
- Larger quantities of REEs followed literature observations concentrating near top and bottom of seam.
- Laterally, some spatial data to verify TREE quantities from hundreds of yards to a few miles.

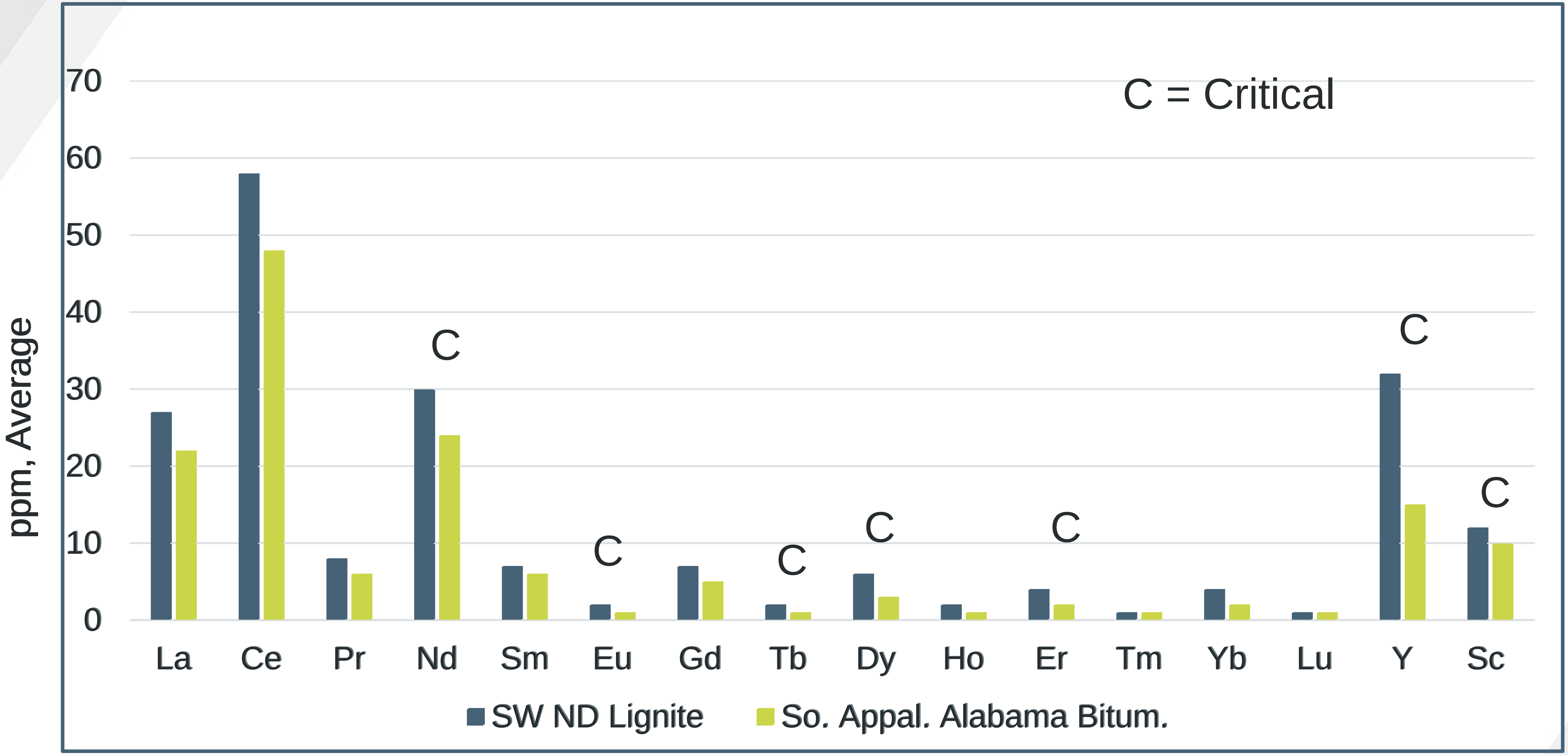


Gascoyne Mine, Harmon lignite seam, 1985

HREE/LREE VERSUS TREE – ALL COAL SAMPLES

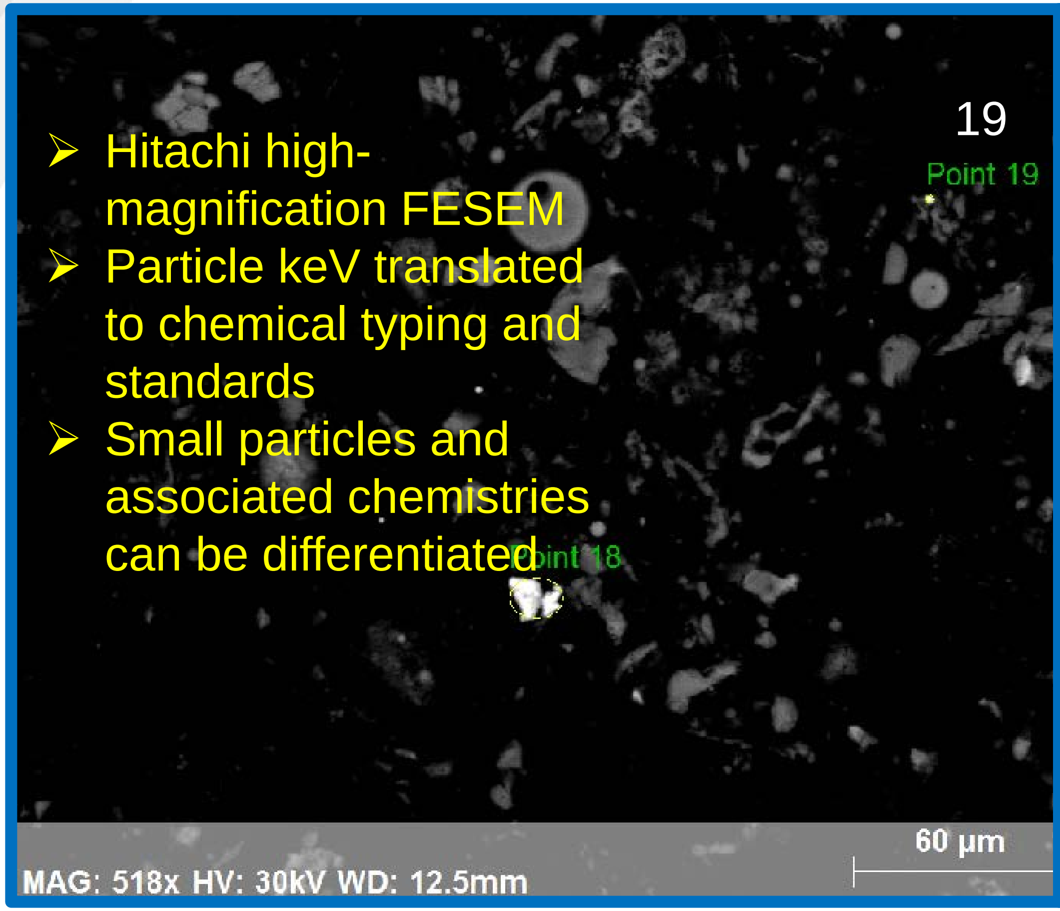


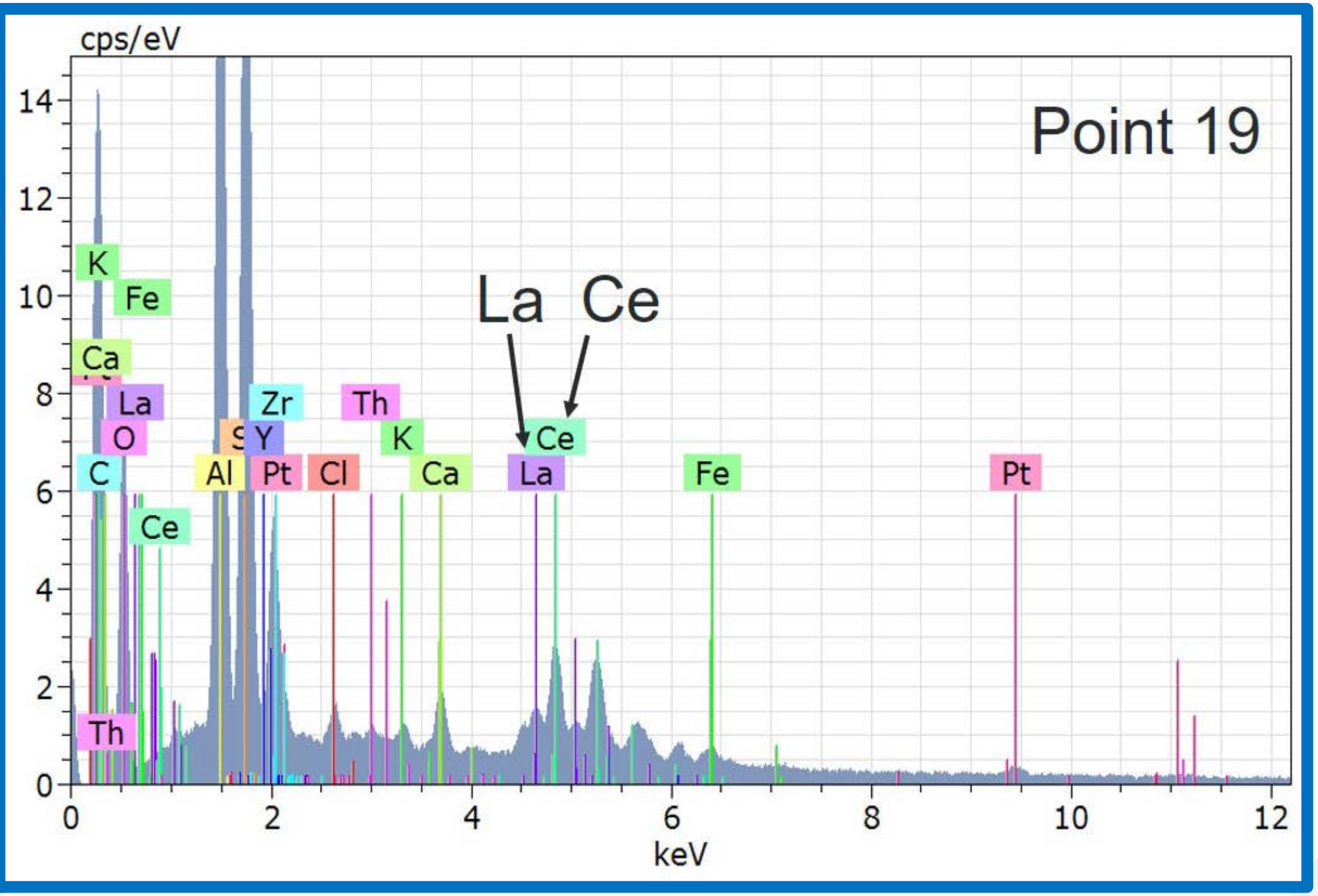
AVERAGE CONCENTRATION OF REES (SELECT COALS)



RESULTS -- CCSEM METHOD DEVISED FOR DETECTION AND QUANTIFIACTION OF REEs IN COALS AND ASH

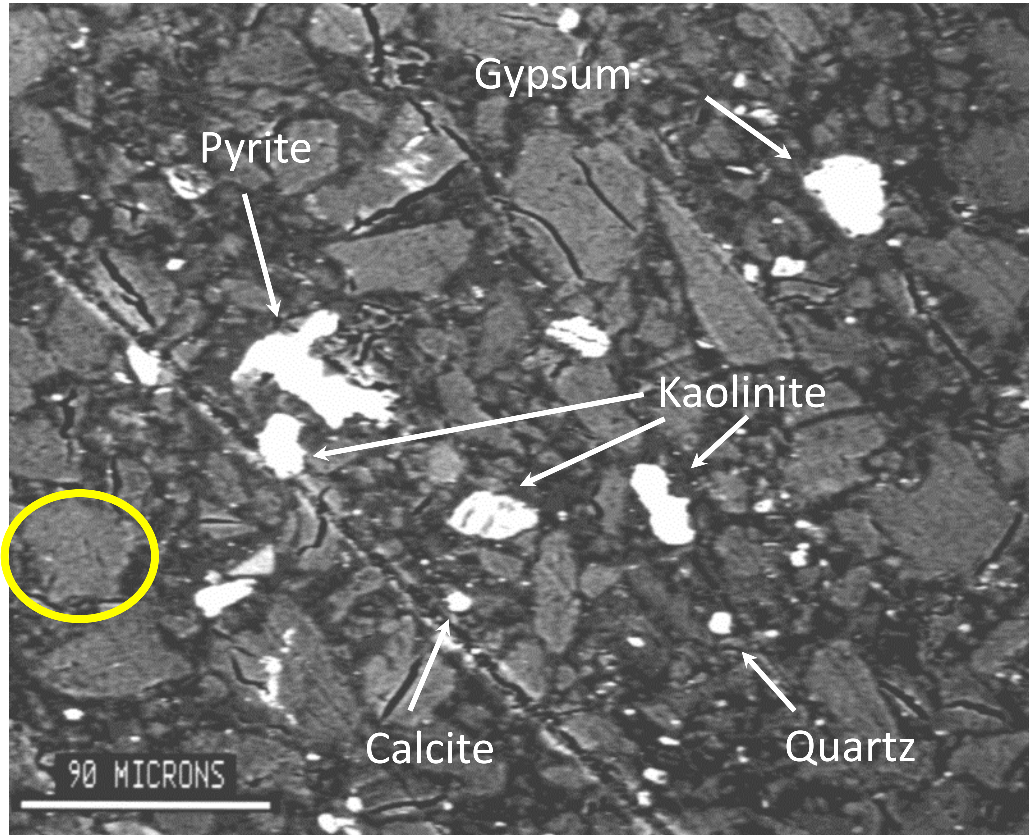
- Hitachi high-magnification FESEM
- Particle keV translated to chemical typing and standards
- Small particles and associated chemistries can be differentiated





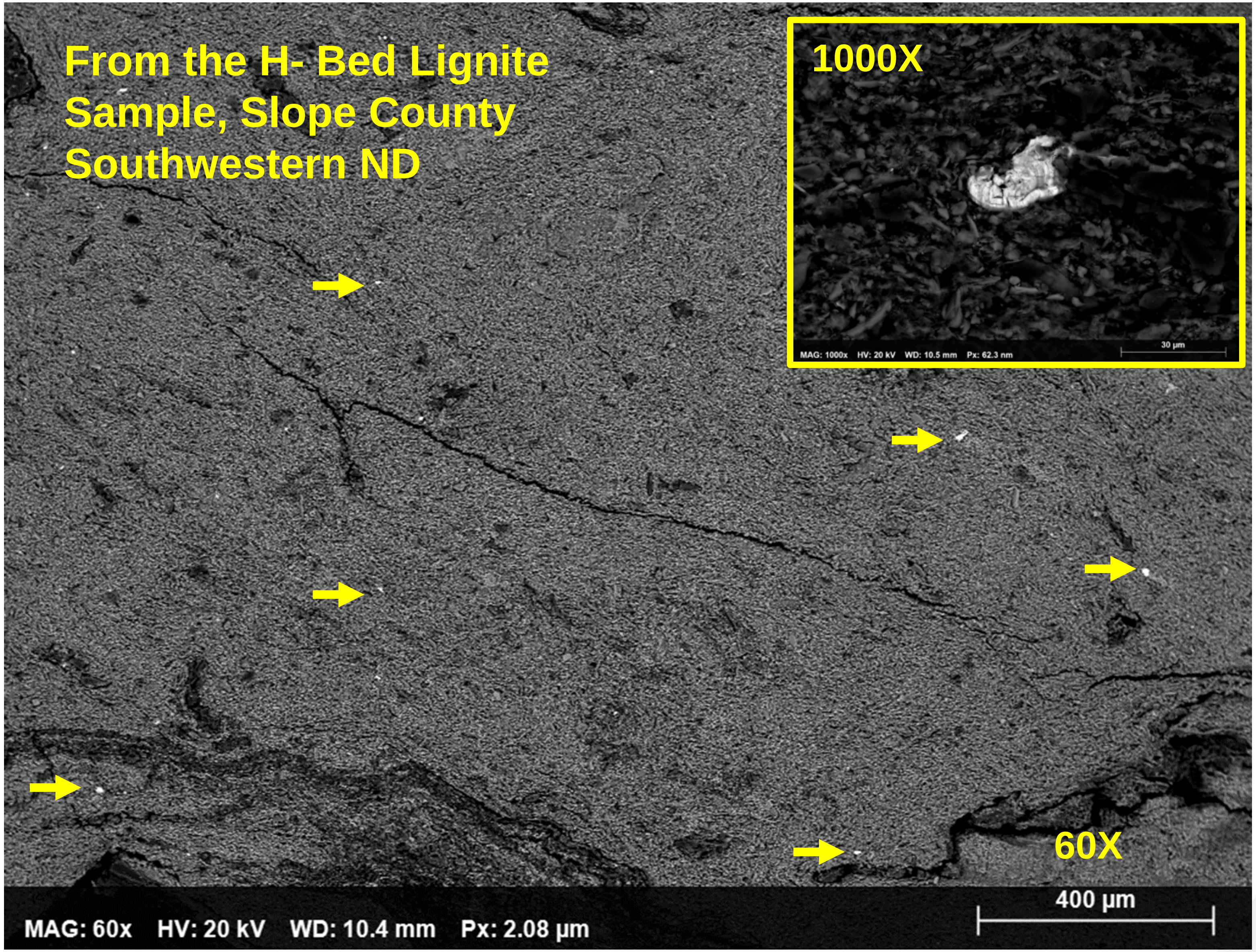
SMALL INDIVIDUAL PARTICLES NOT VISIBLE WITH OLDER SEM SYSTEMS

Low-rank coals will have abundant alkali in association with organic functional groups.



HITACHI FE SEM

- Automated detection, identification, and quantification of REE-rich phosphate particles in coal
- A significant fraction of the REEs associated in the organic structure in the coal
- Very fine bright spots are La, Ce, Nd, Gd particles



NEXT UP -- COALS FOR GRAVITY SEPARATION

Description	% Ash, dry	Total REE + Y + Sc, ppm (dry coal)	HREE/LREE
ND Lignite – Hanson	39	370	0.38
ND Lignite – H-Bed	60	1026	0.2
ND Lignite – H-Bed	26	398	0.35
ND Lignite – Twin Butte	30	365	0.89
ND Lignite – Hagel	29	233	0.45
ND Lignite – Harmon	28	439	0.46
TX Lignite – Olmos	21	257	0.32
WY Subbit. – Anderson	21	189	0.34
MT Lignite – Pust	54	150	0.85
KY Bitum.	6	126	0.3

RESULTS – STATUS OF THE RRIS

- Sample materials and specific round-robin instructions have been assembled.
- Sample info was sent in January 2019.
- Results due March 29, 2019.
- Four coals, three fly ash, clay parting, shale, anthracite AMD, and mine waste
- Three samples are NIST SRMs.

Sample Type	Origin	~TREE, ppm, dry mass basis	~ Ash Content, %
Lignite coal	North Dakota/Harmon Seam	400	25–30
Subbituminous coal	Wyoming/Powder River Basin	200	20–22
Bituminous coal	Central Appalachian	125	6–8
Bituminous fly ash	Kentucky power plant/Central Appalachian coal	700	98–100
Subbituminous fly ash	Wisconsin power plant/Powder River Basin coal	400	98–100
Clay parting	Texas/subbituminous	280	95–98
Acid mine drainage sludge	Pennsylvania/Central Appalachian anthracite	200	50-55
Bituminous fly ash	NIST SRM – Pennsylvania power plant/bituminous	>600	90–93
Shale	USGS SRM – Pennsylvania Bush Creek shale	315	90–93
Bituminous coal	NIST SRM – Pennsylvania bituminous	50	6–8
Mine waste material	NIST SRM – Central Colorado	200	88–90

[1] To be determined

[2] Added after Final RRIS Plan was submitted. Pending approval from DOE.

RRIS PARTICIPATING LABORATORIES

- 15 laboratories
- Statistical analysis of reported data:
  - **Repeatability** (within laboratory variability)
  - **Reproducibility** (between laboratory variability)
  - **Bias** (deviation from known values of standard reference materials)
  - **Variability** (Method to method

Laboratory	Accreditation/ Certification	Procedure Method D6357-11	Procedure Method D4503-08
Act Labs	X		X
Duke University		X	
Geochemical Testing, Inc.	X	X	X
Hazen Research, Inc.	X		X
Kentucky Geological Survey		X	
McCreath Laboratories	X	X	X
Nexus Geos/University of Nebraska (Tetra Tech)			X
Ohio State University		X	
Research Triangle Institute			X
SGS	X	X	
Standard Laboratories, Inc.	X	X	X
University of Iowa		X	
UND-EERC		X	X
Southern Research - Water Research Center		X	
University of Missouri Research Reactor Center		NAA	

INSIGHTS: INDUSTRY, MARKETS, NEEDS

- New potential resources for REEs and information on the association of these REEs in coal beds could impact future new domestic markets
- 648 samples mostly from western resources and specific focus on ND lignite
- 259 samples with TREEs >= 300 ppm dry **ash** basis
- All but one of the western sources have existing mine infrastructure and energy utilization

INSIGHTS: INDUSTRY, MARKETS, NEEDS

- Western low rank coals
  - Evaluation of the occurrence of small REE-rich mineral inclusions in the organic matrix of ND and MT lignites may give insights on extraction.
- Eastern higher-rank coals: new data, especially in southern Appalachian bituminous coals show REE potential in combustion ash.
- Data for estimation of regional REE reserves (ongoing)
- Critical mode of occurrence and association determinations may help devise methods for economic extraction.

CONCLUDING REMARKS

- Nearly 650 samples of coal and coal-related materials examined as potential new sources of high REEs; a strategic goal of DOE.
- Confirmation of REE economic potential in select ND lignites and southern Appalachian bituminous coals.
- Remaining contract milestones/deliverables: complete all characterization, complete final report, and provide quality data set for DOE NETL EDX.
- On target progress of a round robin interlaboratory study for the preparation and analysis of REE bearing materials to aid in accurate REE resource assessments and commercial development.
- Advanced SEM methods developed and demonstrated to aid in designing better REE identification, quantification, and extraction.

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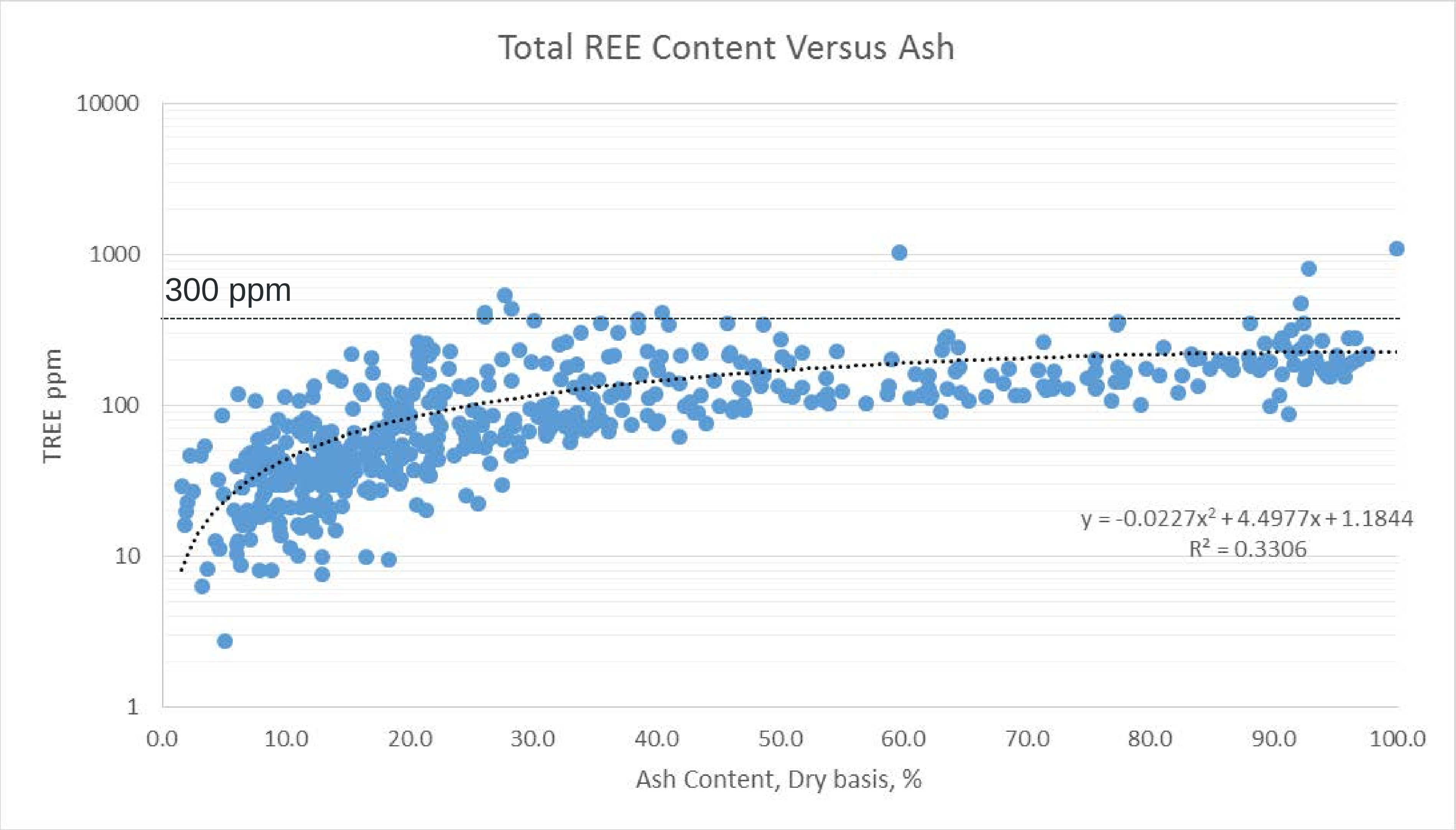
CONVENTIONS

- HREE: heavy rare earth element
- LREE: light rare earth element
- Scandium is not used in the HREE/LREE ratio calculation.
- TREEs: total rare-earth elements (includes Sc + Y)

Element	Symbol	Atomic No.	Crustal Abundance, ppm	Economic Class
Light Rare-Earth Elements				
Lanthanum	La	57	39	Uncritical
Cerium	Ce	58	66.5	Excessive
Praseodymium	Pr	59	9.2	Uncritical
Neodymium	Nd	60	41.5	Critical
Samarium	Sm	62	7.05	Uncritical
Europium	Eu	63	2.0	Critical
Heavy Rare-Earth Elements				
Gadolinium	Gd	64	6.2	Uncritical
Terbium	Tb	65	1.2	Critical
Dysprosium	Dy	66	5.2	Critical
Holmium	Ho	67	1.3	Excessive
Erbium	Er	68	3.5	Critical
Thulium	Tm	69	0.52	Excessive
Ytterbium	Yb	70	3.2	Excessive
Lutetium	Lu	71	0.8	Excessive
Yttrium	Y	39	33	Critical
Nonclassified Rare-Earth Element				
Scandium	Sc	21	22	Critical

TREE VERSUS ASH CONTENT (all samples)



NEXT STEPS – GRAVITY SEPARATIONS AND FINISH ALL CHARACTERIZATION

- Strategic selection of ten samples for float–sink separation to evaluate concentration impacts; aid in mode of occurrence determination, and gain insights on extraction/recovery.
- In low-rank coals, REEs are concentrated in the organic fraction, so by removing the higher-density, mineral-rich fraction of the coal, the REEs can be substantially enriched in the remaining organic-rich fraction.
- In high-rank coals, the REEs are concentrated in the higher-density mineral matter.
- The float–sink techniques to be used are outlined in ASTM D4371 (2012) Standard Test Method for Determining the Washability Characteristics of Coal.
- The separations will be done by a commercial lab (TBD).
- Characterization is pending for gravity fractions.

INSIGHTS: INDUSTRY, MARKETS, NEEDS

- Western low rank coals
  - Evaluation of the occurrence of small REE-rich mineral inclusions in the organic matrix of ND and MT lignites may give insights on extraction.
- Eastern higher-rank coals: new data, especially in southern Appalachian bituminous coals show REE potential in combustion ash.
- Data for estimation of regional REE reserves (ongoing)
- Critical mode of occurrence and association determinations may help devise methods for economic extraction.

INSIGHTS: INDUSTRY, MARKETS, NEEDS

- Western low rank coals
  - Evaluation of the occurrence of small REE-rich mineral inclusions in the organic matrix of ND and MT lignites may give insights on extraction.
  - The value of samples with TREEs >300 that show a HREE/LREE ratio > 1, may need further clarification, since very few samples fit this criteria in the study.
- Eastern higher-rank coals: new data, especially in southern Appalachian bituminous coals show REE potential in combustion ash.
- Estimation of regional REE reserves (ongoing) holds promise for potential new reserves.
- Critical mode of occurrence and association determinations may help devise methods for economic extraction.