

UNIVERSITY OF NORTH DAKOTA SAMPLING, CHARACTERIZATION, AND ROUND-ROBIN ANALYSES OF DOMESTIC U.S. COAL-BASED RESOURCES CONTAINING HIGH RARE-EARTH ELEMENT (REE) CONCENTRATIONS

2018 U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Rare-Earth Element Annual Meeting, Pittsburgh, PA, April 10, 2018



PROJECT SUMMARY

Team:

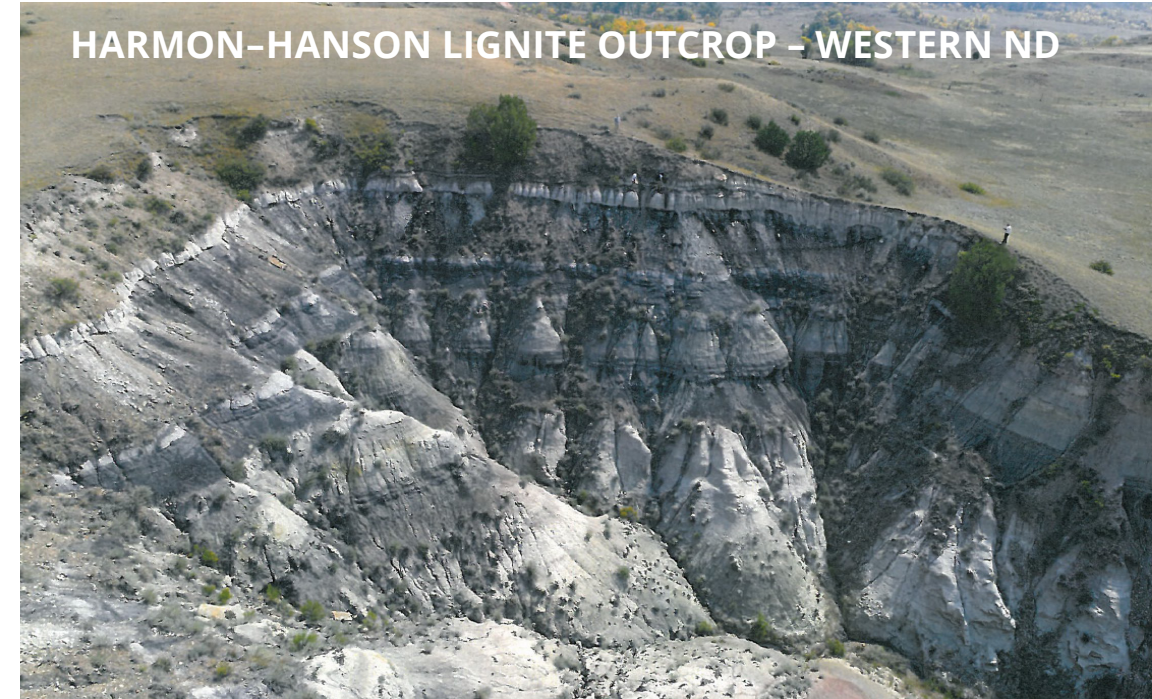
- University of North Dakota (UND) Energy & Environmental Research Center (EERC) and Institute for Energy Studies (IES)
- University of Kentucky (UK) Center for Applied Energy Research
- Kentucky Geological Survey (KGS)
- North Dakota Geological Survey (NDGS)
- Microbeam Technologies Inc. (MTI)

Partners: Coal and utility industry companies

DOE CONTRACT DE-FE0029007: Oct. 2017 – Sept. 2019
Vito Cedro III, DOE Contracting Officer's Technical Representative
Mary Anne Alvin, DOE Rare-Earth Element Technology Manager
Chris J. Zygarić, EERC Principal Investigator

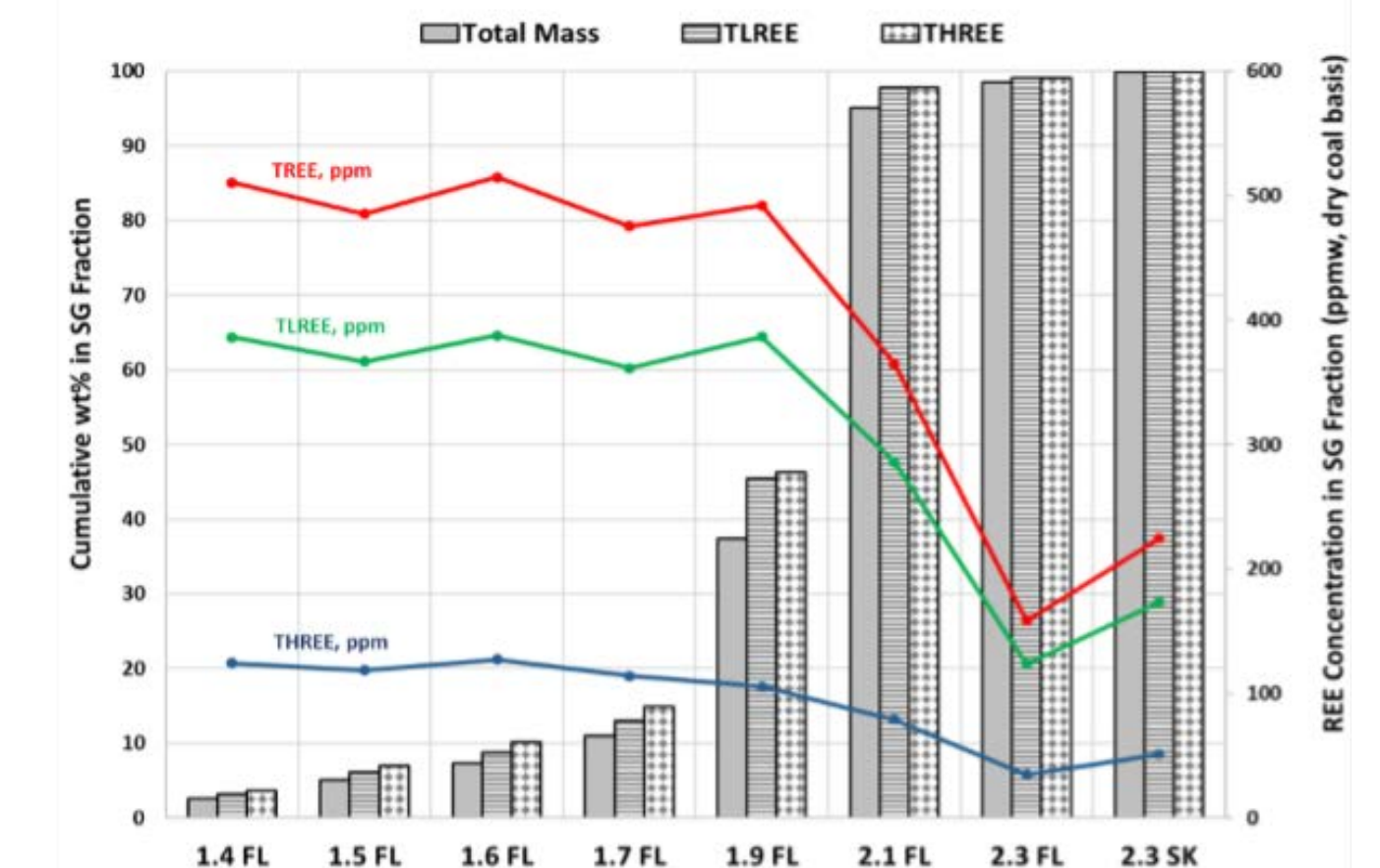


REEs: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and transition elements scandium (Sc) and yttrium (Y).



SAMPLE PREP, CHARACTERIZATION, AND MODE OF OCCURRENCE ANALYSES

- ASTM prep and analyses.
- Inductively coupled plasma-mass spectrometry (ICP-MS) and ICP-OES (optical emission spectroscopy) for REEs.
- Mode of occurrence analyses:
 - Field emission scanning electron microscopy (SEM) for REE analysis.
 - Selected float-sink separation and modified chemical fractionation.
- Previous work shows 85%–95% organic association of REEs in ND lignites.
- REEs in coordination complexes.
- Small fraction of REEs in silicates/clays.



SCOPE OF WORK

Identify specific sources of coal and coal-related materials that have potentially >300 ppm on a dry mass basis of REEs based on databases, literature, and input from coal-mining companies.

Perform sample collection, preparation, initial analysis of coal and coal-related materials that are likely to exceed >300-ppm REEs.

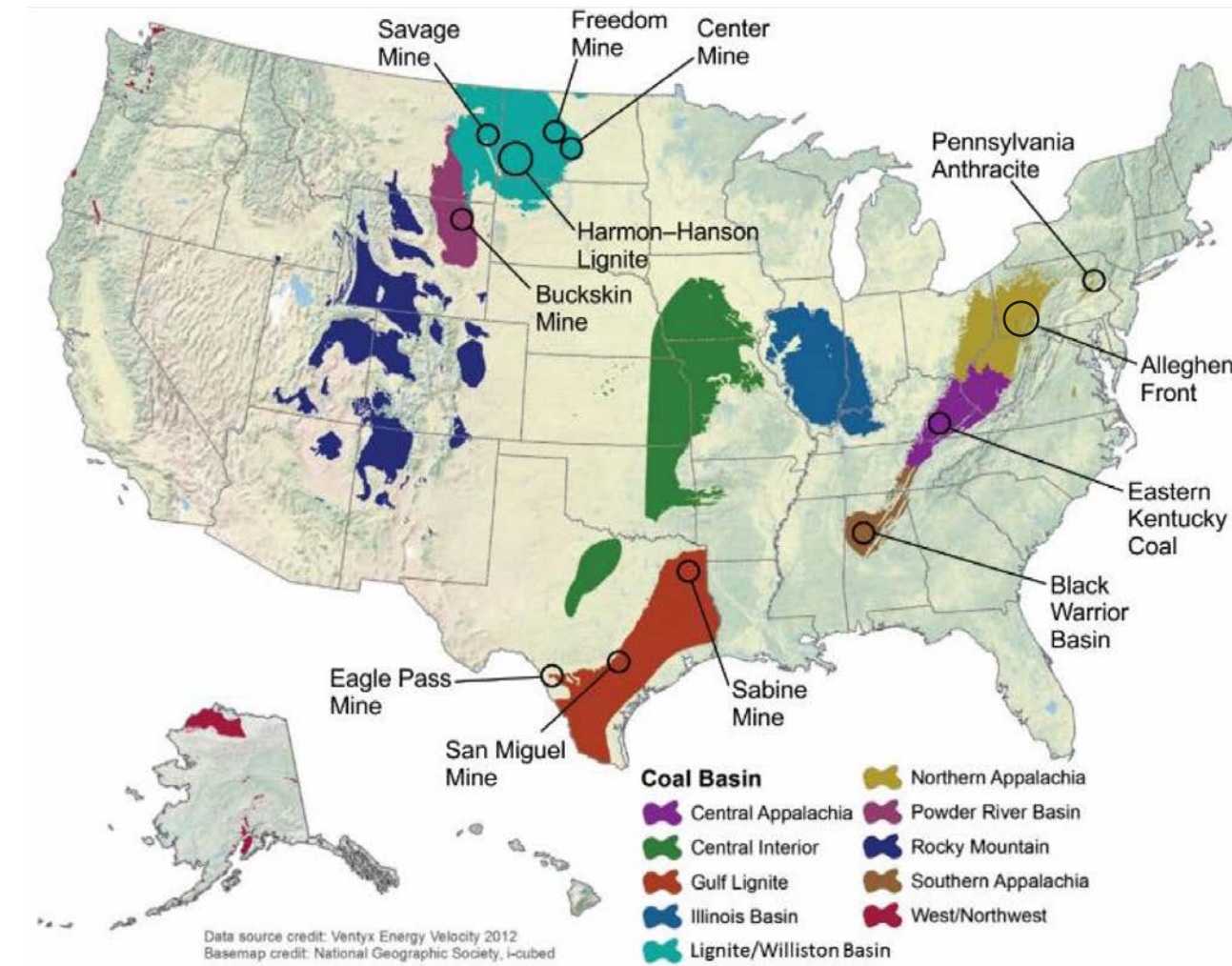
Characterize nearly 600 samples for REEs using conventional and advanced analyses.

Coordinate a round-robin interlaboratory study (RRIS) as an efficient, statistically aimed evaluation of REE quantification at select laboratories.

Determine lab-to-lab and method-to-method variability.

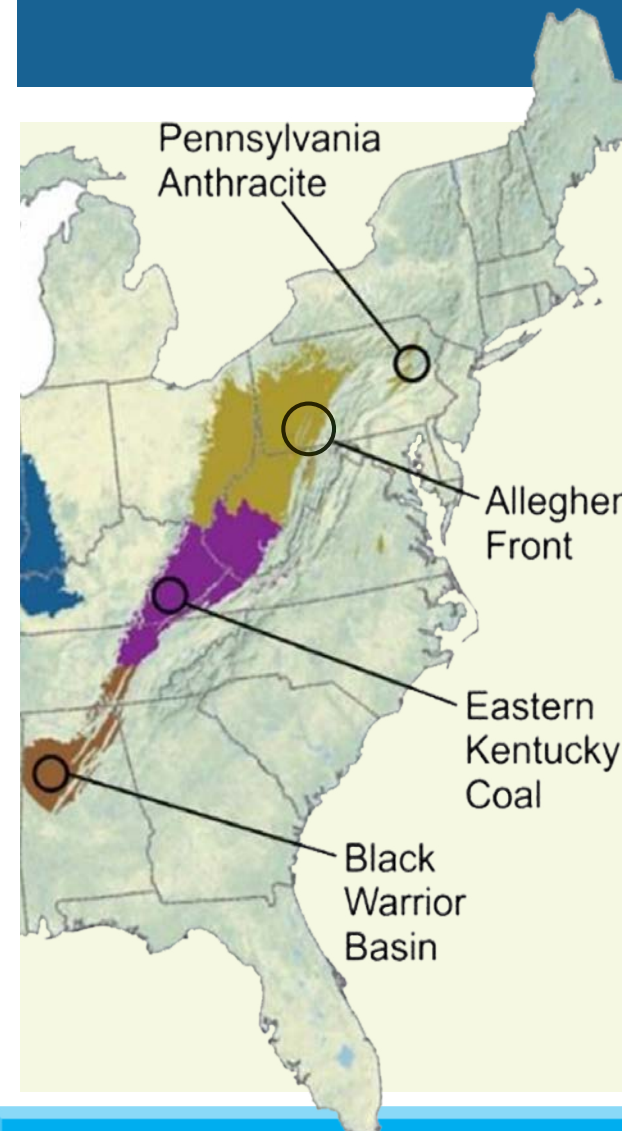
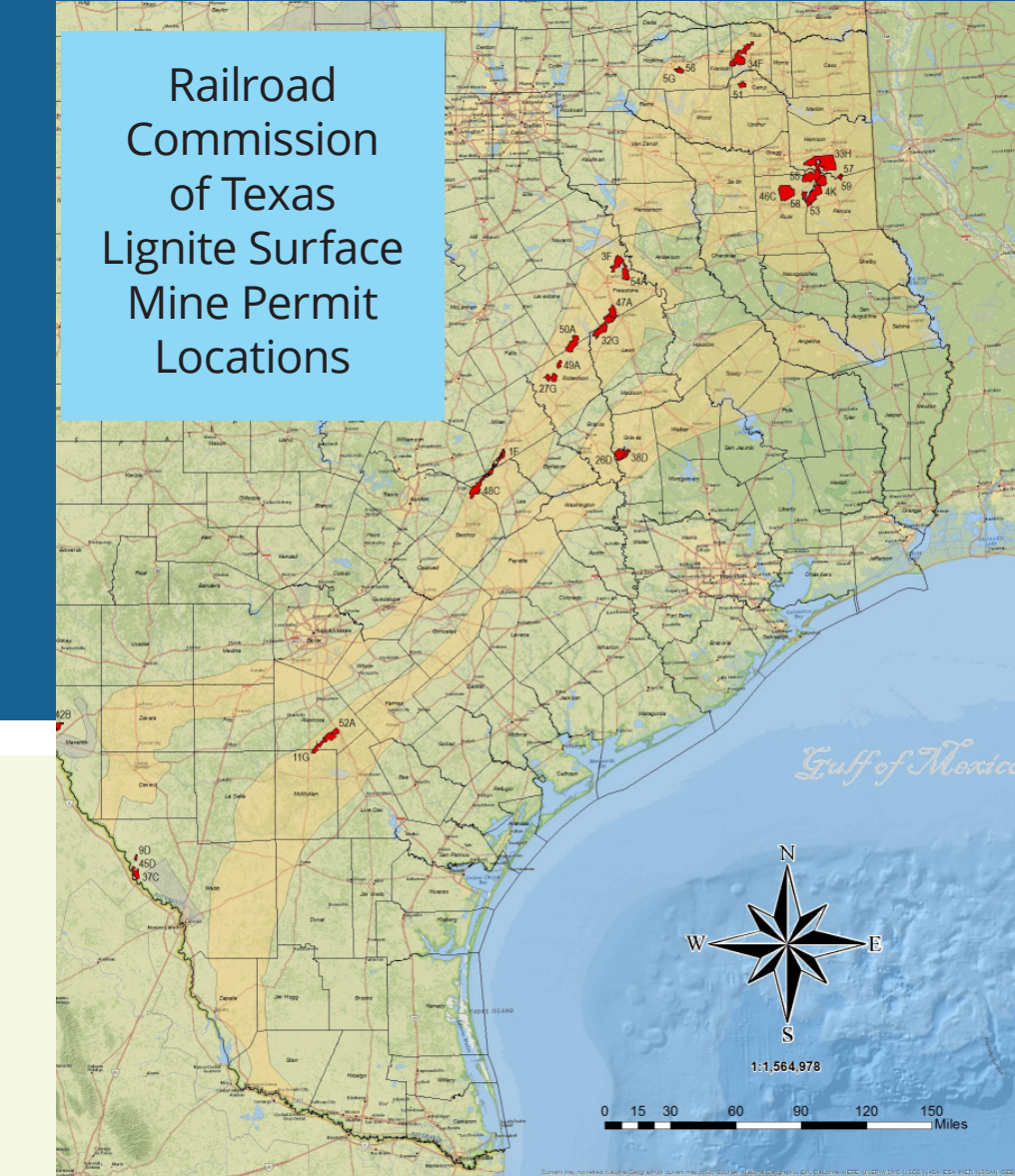
Estimate or update estimates of the total domestic REE reserves using the characterization results for each targeted region.

Upload sample data to DOE NETL EDX.



TEXAS GULF COAST SAMPLING COAL TARGETS (10%)

- CoalQual database information.
- 300-ppm total REE potential in lignite and subbituminous coals.
- Several samples with 600+ total REEs.
- Partings with volcanic ash origins.
- Presence of U and Th possible indicators of REEs.



EASTERN U.S. SAMPLING TARGETS (10%)

- Pennsylvanian anthracite fields with hydrothermal metamorphism.
- Western Pennsylvania geochemical alteration.
- Eastern KY – Coals below the Fire Clay known for high Cl, As, Hg, other elements indicating fluid flow and potential REEs.
- Alabama coalfields – Bituminous coal with hydrothermal metamorphic REE deposits.
- Various possible acid mine drainage (AMD) samples throughout.

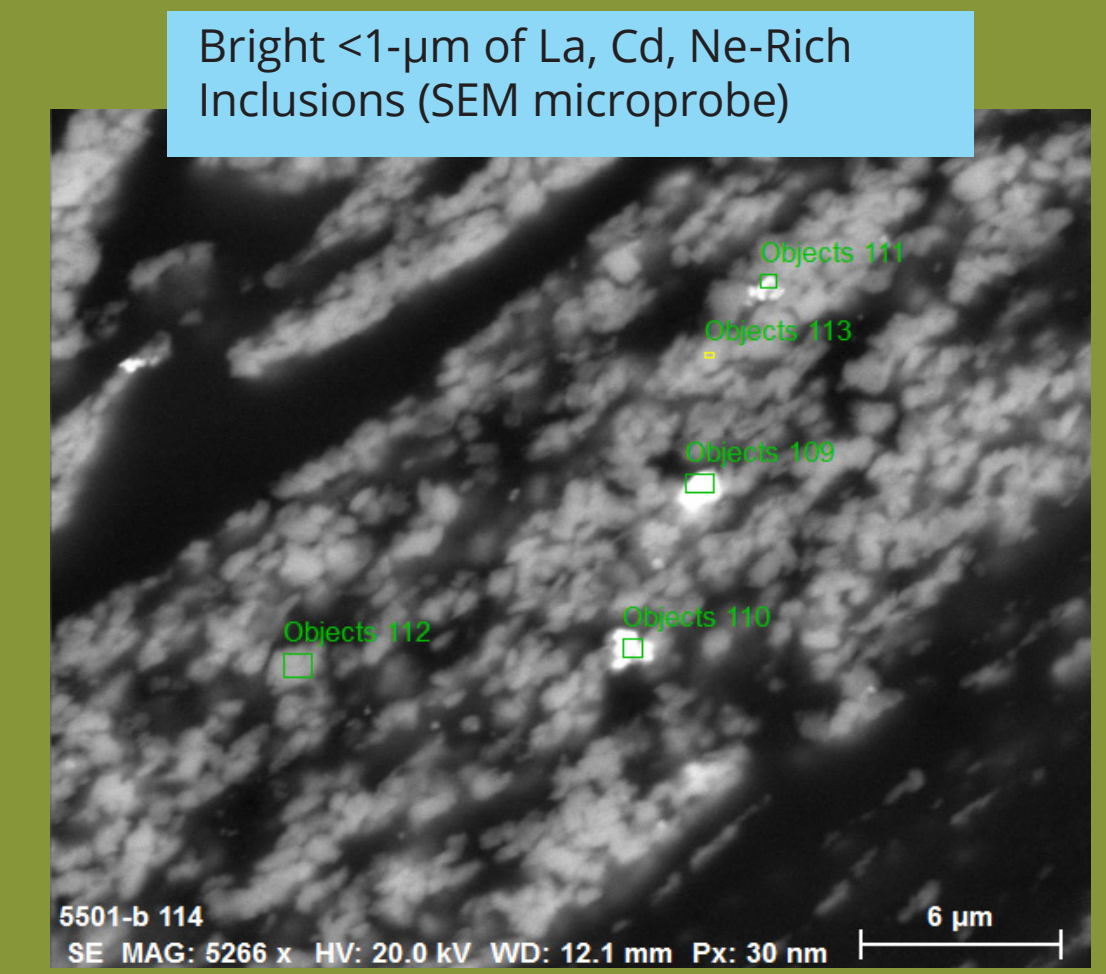
MODES OF OCCURRENCE AND RESERVE ANALYSIS

Modes

- Terrigenous, tuffaceous, infiltrational, and hydrothermal (eastern U.S. coals only).
- Diagenesis: slow transformation and redistribution of organically associated elements (western U.S. coals only).

Reserve Analysis

- Calculate REE reserves (>300 ppm) using USGS methods.
- Preliminary estimates for western coals: 10 million tons of REEs in ND, MT, and WY coals.



PROJECT TASKS

- Perform Project Planning and Management
- Identify Proposed Sources, Field Samples, and Procedures for Sampling and Field Preparation/Preservation of Samples
- Perform Sampling
- Perform Sample Preparation and Characterization in the Laboratory
- Identify Laboratories and REE Samples to Be Used in the RRIS
- Develop the RRIS Plan
- Obtain and Distribute Samples, Calibration Standards, and Procedures to Laboratories Participating in the RRIS
- Perform the RRIS
- Provide Project Reporting to NETL and Sample Retention



WESTERN U.S. COAL SAMPLING TARGETS (80%)

Center Mine – Kinneman Creek Coal

- High REE content in lignite, roof, and partings.
- Only La, Ce, Sm, Eu, and Yb analyzed with high levels of Th and U.
- Volcanic ash-derived clay tonstein overlay lignite.

Freedom Mine – Beulah-Zap Coal

- 5 seams interbedded with nonorganic clastics.
- Rutile in quartz, zircon, and clays of volcanic origin.
- Total REE contents of 150–200 ppm observed.

Harmon – Hanson Coal

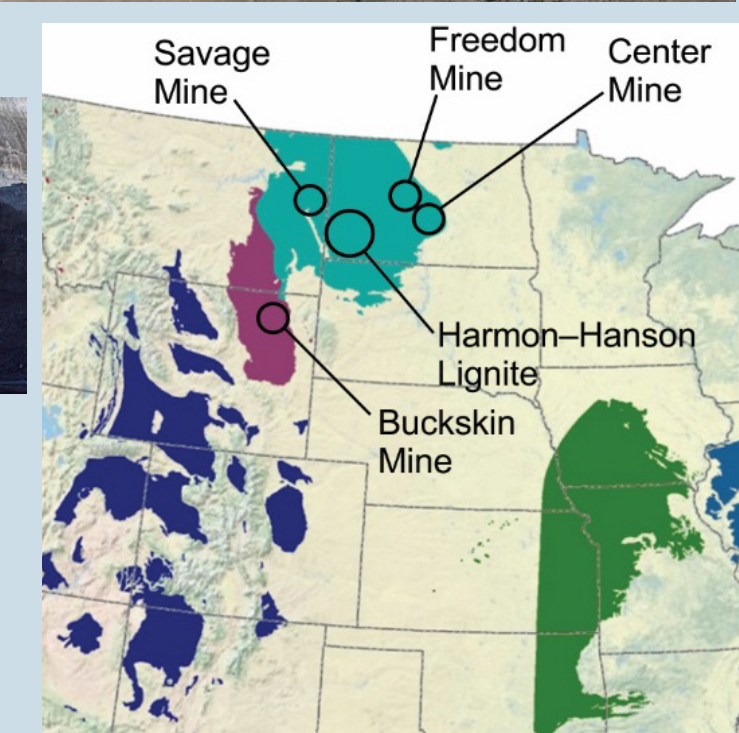
- Outcrop samples only, mine closed.
- NDGS revealed total REE >600 ppm.
- 1980s research shows volcanic ash.

Savage Mine – Pust Coal

- Limited characterization data.
- Part of the Upper Fort Union Formation.
- Volcanic ash glass in shale beds near the coal seam.

Buckskin Mine – Anderson-Canyon Coal

- Powder River Basin, Fort Union Group.
- USGS reports 200–300-ppm total REEs.
- REEs in crandallite and apatite coal minerals.
- Volcanic ash deposits in the Anderson coal bed.



Western Coal Regions					
Coal Basin	Sample Type	Location/Mine Name	Mine Owner	Total No. Samples	Formation
Williston Basin	Lignite	Center Mine, ND	BNI Coal	90	Kinneman Creek
	Lignite	Freedom Mine, ND	North American Coal (NA Coal)	90	Beulah-Zap
	Lignite	Southwest ND/old Gascoyne lignite	No active mine	90	Harmon-Hanson
	Lignite	Savage Mine, MT	Westmoreland Coal Co.	90	Pust
Powder River Basin	Fly ash/bottom ash	TBD ¹	TBD	20	TBD
	Subbituminous coal	Buckskin Mine, WY	Kiewit Coal	80	Anderson-Canyon
	Fly ash/bottom ash	TBD	TBD	6	TBD
Gulf Coast Lignite	Lignite	Texas	Undisclosed	25	Undisclosed
	Lignite	Texas	Undisclosed	13	Undisclosed
	Subbituminous	Texas	Undisclosed	12	Undisclosed
	Fly ash/bottom ash	TBD	TBD	6	TBD
Eastern Coal Regions					
Northern Appalachia	Anthracite coal	Pennsylvania	Undisclosed	12	Llewellyn and Pottsville
	Bituminous	Allegheny Front, PA	TBD	12	Allegheny
Central Appalachia	Bituminous	East Kentucky Coals	TBD	12	Breathitt
Southern Appalachia	Bituminous	Black Warrior Basin	TBD	12	Pottsville
	TBD	TBD	TBD	8	TBD
	Fly ash/bottom ash	TBD	TBD	4	TBD
	AMD/sludge	TBD	TBD	4	TBD

SOURCES, FIELD SAMPLES, AND PREPARATION

- Source locations (literature, mines, etc.).
- Strip mine channel samples.
- Coal mine exploratory core samples.
- Outcrops.
- Sample banks UND, UK, Penn State.
- Mine breaker samples.
- AMD (eastern coals).
- 582 samples of coal and coal-related materials.



IDENTIFY LABORATORIES AND REE SAMPLES TO BE USED IN THE RRIS

RRIS Laboratories

- 12–14 labs total TBD.
- Target labs with proficiency in either ASTM D4503 (borate fusion) or ASTM D6357 (acid digest) or both.
- University of Missouri Research Reactor Center identified for neutron activation analysis.
- Other labs TBD.

RRIS Sample Candidates

- 3 coals (lignite, subbituminous, bituminous).
- 2 sediments (1 – high-concentration REE, 1 – low).
- 1 fly ash.
- 1 bottom ash.
- 1 AMD sludge
- 2 standard reference materials (NIST and USGS materials).

ROUND-ROBIN INTERLABORATORY STUDY

- Moisture, wt%.
- Ash, wt%.
- Individual triplicate results for 14 lanthanides + Y + Sc reported on a mg/kg (ppm), dry sample basis.
- Calibration information.
- Requested turnaround time ≈ 2 months.
- Statistical analysis of reported data using ASTM E 691.
- Repeatability (within laboratory variability).
- Reproducibility (between laboratory variability).
- Bias (deviation from known values of standard reference materials).
- Method-to-method variability.

SUMMARY OF RESULTS TO DATE

- All management, sampling, preparation, and characterization plans completed.
- Acquiring samples.
- Harmon-Hanson lignite outcrops sampled by NDGS and UND show 200–400-ppm dry-mass-basis and 480–980-ppm dry-ash-basis total REEs.
- Advanced fractionation and SEM analyses initiated.
- Round-robin laboratories being contacted.

CONTACT INFORMATION

Energy & Environmental Research Center, University of North Dakota
15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018

Chris J. Zygarić
Associate Vice President for Strategic Projects
701.777.5123 (phone)
701.741.7345 (cell)
czygarlicke@undeerc.org

www.undeerc.org