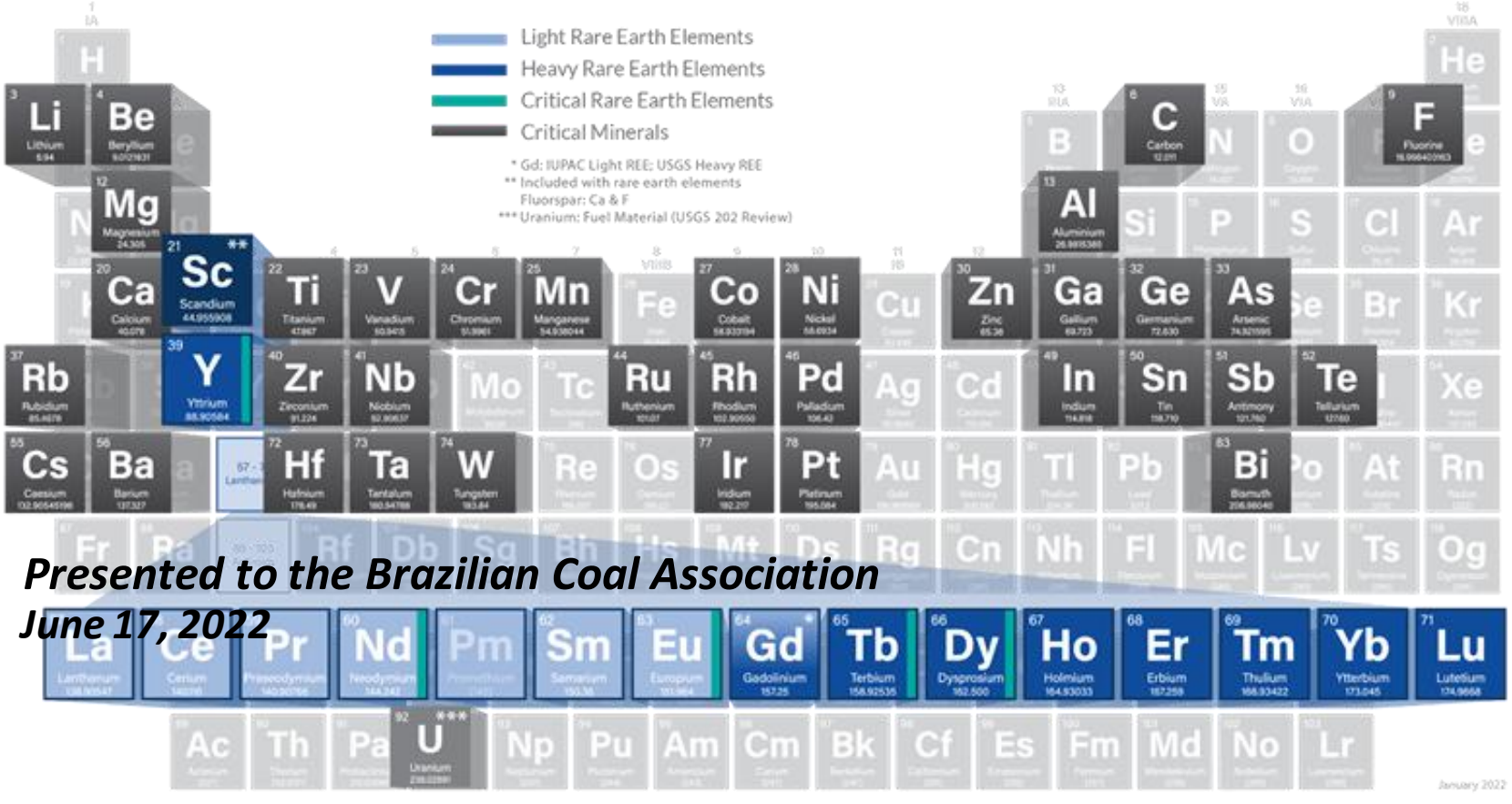
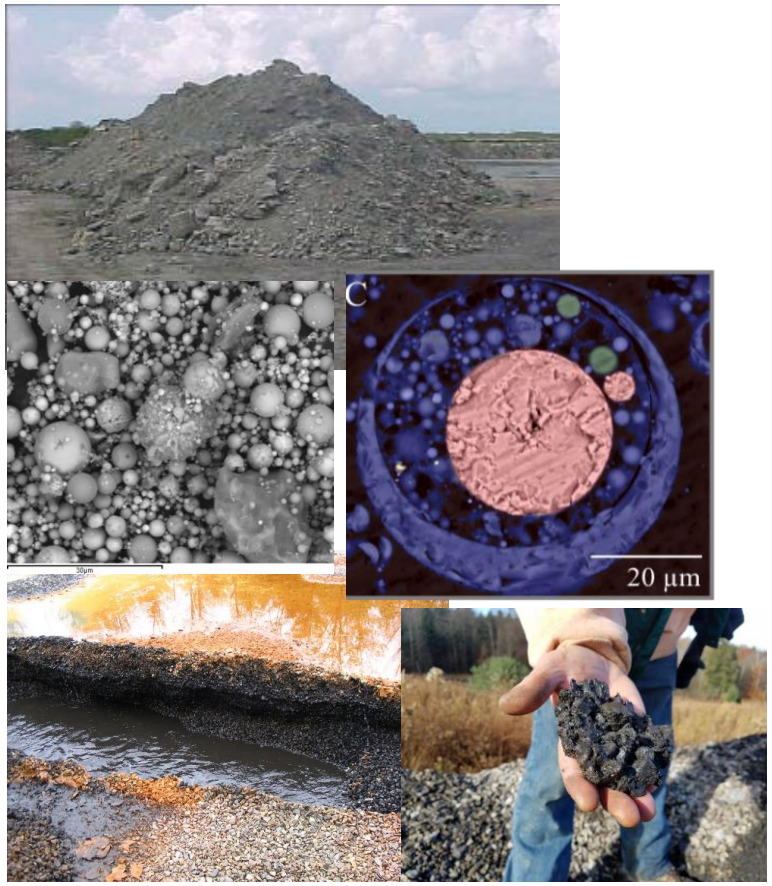
Rare Earth Element/Critical Mineral (REE/CM) Recovery from Coal Byproducts and Acid Mine Drainage

Dr. Mengling Stuckman
Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY





Presented to the Brazilian Coal Association
June 17, 2022

Disclaimer

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Critical Minerals in Fossil Energy Wastes

55 Minerals Identified to be Critical to National Security (U.S. Dept. of Interior)

"Mineral commodities that have important uses and no viable substitutes, yet face potential disruption in supply, are defined as critical to the nation's economic and national security."

Mineral	Top producer	Top supplier	Notable example application	Potential fossil energy feedstocks
Aluminum	China	Canada	Aircraft, power transmission lines, alloys	AMD solids, fly ash
Cobalt	*Congo	Norway	Jet engines, rechargeable batteries	AMD solids, drill cuttings
Lithium	Australia	Chile	Rechargeable batteries, Al-Li alloys for aerospace	AMD solids, Produced waters
Manganese	China	South Africa	Aluminum and steel production, lightweight alloys	AMD solids
Rare earth elements	China	China	Catalyst, magnets, aerospace guidance, laser, fiber optics	AMD solids, fly ash

https://www.usgs.gov/news/interior-releases-2018-s-final-list-35-minerals-deemed-critical-us-national-security-and

*Democratic Republic of the Congo

What if These Coal By-Products…

American Subsidy: Valorization of Critical Minerals from Fossil Energy Waste Streams


Coal


Refuse


Fly Ash


Acid Mine Drainage (AMD)

COULD BE PROCESSED TO…


Produce Rare Earth Elements


Fortify National Security


Produce Feedstock for Advanced Materials


Produce Clean Water

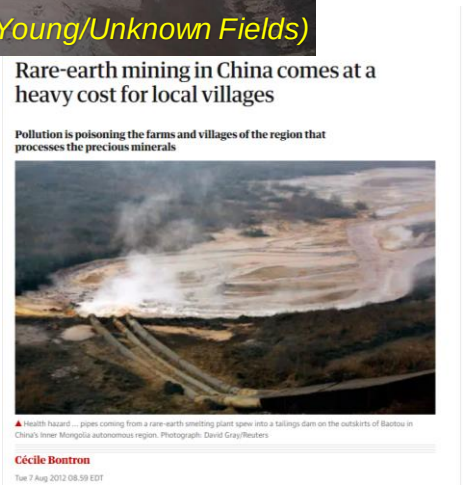
1. amrclearinghouse.org, 2. fondriest.com, 3. defenseimagery.mil, 4. netl.doe.gov, 5. energy.gov

REE Mining - Large Environmental Footprint

Environmental Impacts and Cost drivers:

- Expensive pre-treatment processing
- Strong inorganic acids and bases to crack minerals
- High temperature & pressure process conditions
- Hazards & cost associated with wastes:
  - strong acid wastes containing unwanted elements and radioactive materials (e.g., Thorium, Uranium)
  - High organic solvent use in the purification and separation of REE into individual product streams

https://www.bbc.com/future/article/20150402-the-worst-place-on-earth


Rare-earth mining in China comes at a heavy cost for local villages

Pollution is poisoning the farms and villages of the region that processes the precious minerals

Cécile Bontron

https://e360.yale.edu/features/china-wrestles-with-the-toxic-aftermath-of-rare-earth-mining

https://www.theguardian.com/environment/2012/aug/07/china-rare-earth-village-pollution

Coal-Based Waste Feedstocks

Filling the First Gap to a Domestic REE Supply Chain

- Coal-based feed sources include:
  - Coal (anthracite, bituminous, subbituminous, lignite)
  - Coal refuse
  - **Coal ash (fly ash, bottom ash, ponded ash): est. 8,910 tons REE/year, 95% of REE demand in 2018**
  - **Acid mine drainage (AMD) in Appalachian Basin, 1,120 tons REE/year, 12% of REE demand**
  - Mining underclay and shale

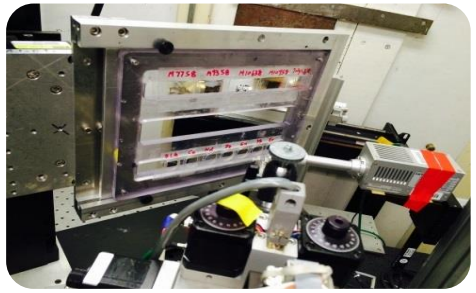
Coal Ash reserve 113 million tons/yr

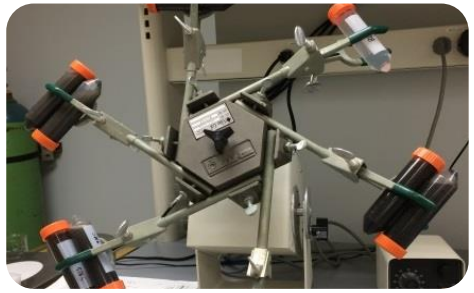
Acid Mine Drainage treatment solids: 18,000 tons/yr

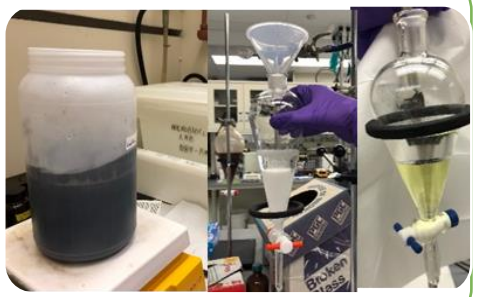
REE speciation in key CCB types
Work Smarter Not Harder

Fundamentally Understanding the Resource

Utilize **characterization** of major REE-hosting solid fractions in different coal waste by products to **innovate targeted extractions** for efficient, sustainable and economical REE recovery.







Bulk Solid Characterization

- More than 2,000 coal waste byproducts in the U.S.

-Elemental Composition

- Mineralogy

Elemental Distribution and Mobility

- **Synchrotron micro-analysis for REE**

Argonne NATIONAL LABORATORY | Advanced Photon Source

SLAC NATIONAL ACCELERATOR LABORATORY

Targeted Leaching

- Sequential extraction:

REE in select coal waste byproducts are extractable

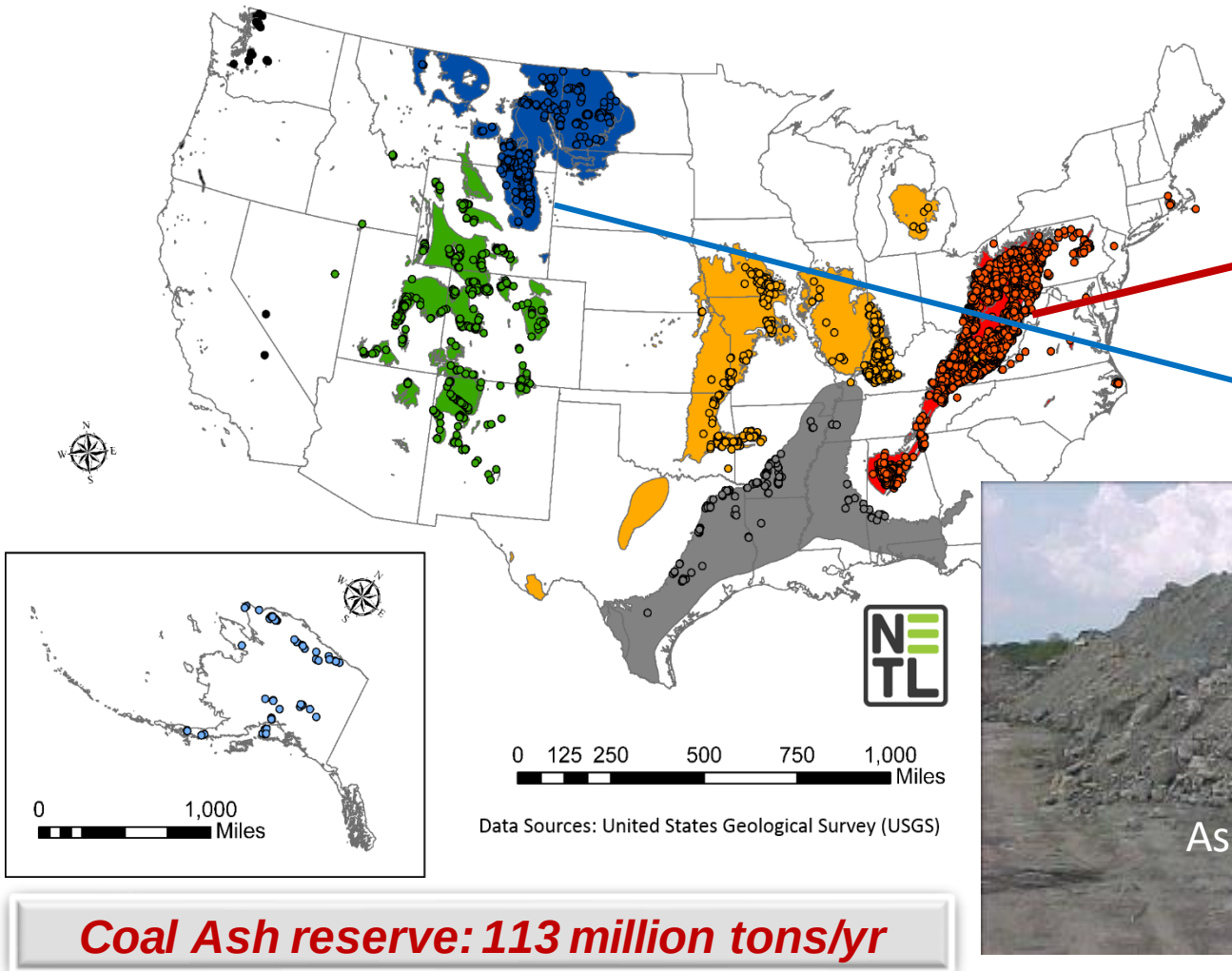
- pH titration

Sustainable solutions

- **Targeted Rare Earth Extraction (TREE)**

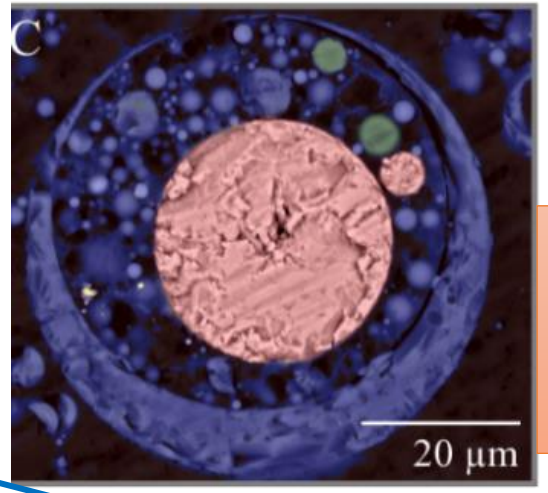
Coal Combustion Ash Wastes

~ 60% Ash is Disposed as Waste (millions of tons/yr)



Coal Ash reserve: 113 million tons/yr

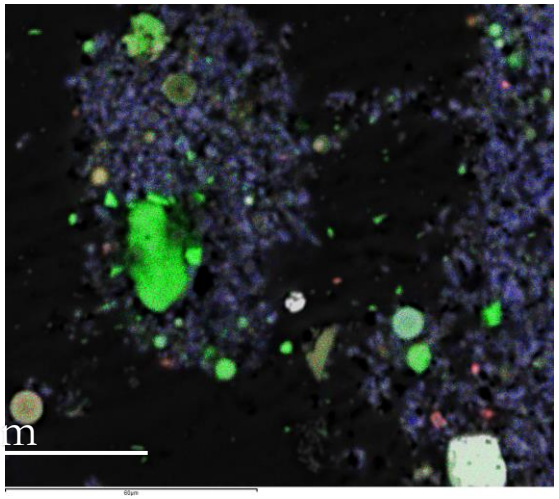
Bituminous coal



SEM BSE image of fly ash particles

amorphous Si-Al -purple
Fe-oxide - red
Ca-oxide - green
REE mineral - yellow

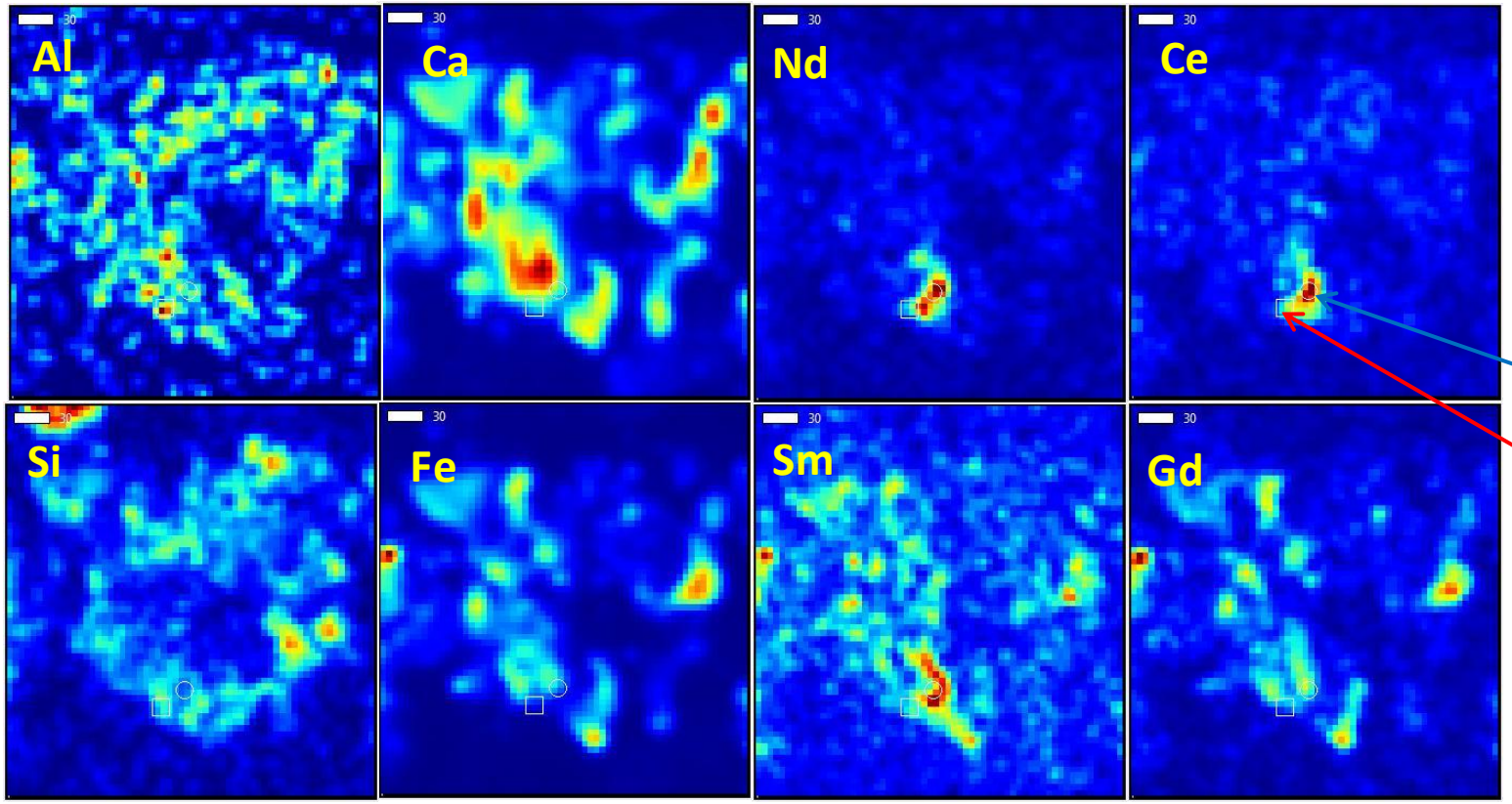
Sub-bituminous and lignite coal (Ca-rich)



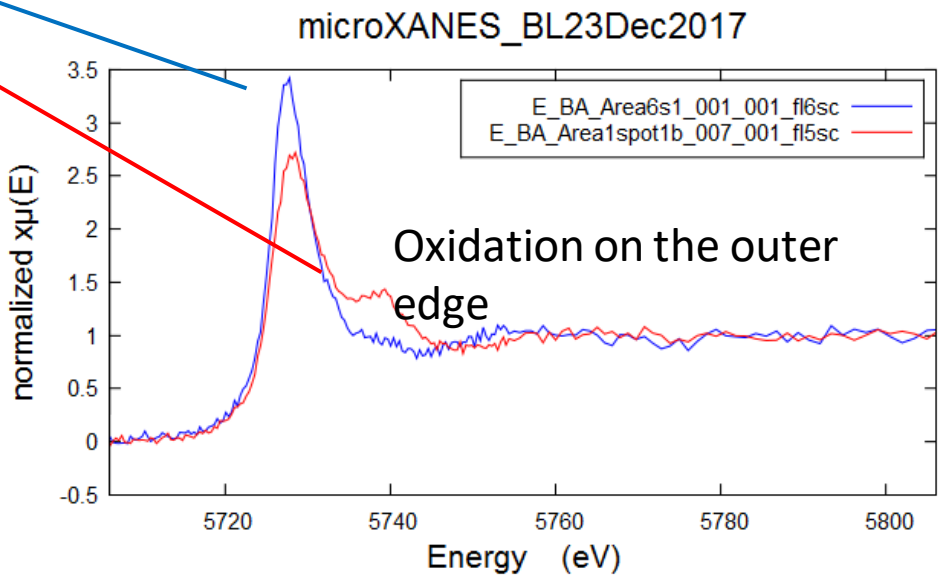
Select Sub-Bituminous Coal Ash: Ce Oxidized in Ca-Rich Glassy Phase

- Example: Ca-, Mg-rich Coal Ash

Light REEs (e.g., Ce, Nd) w/ Ca-rich AlSi, and heavy REEs (e.g., Sm, Gd) w/ Fe



- During coal combustion, Ce diffused into Ca glassy phases: Ce oxidation during coal combustion
  - Ce(III) + O2 = Ce(IV)O2

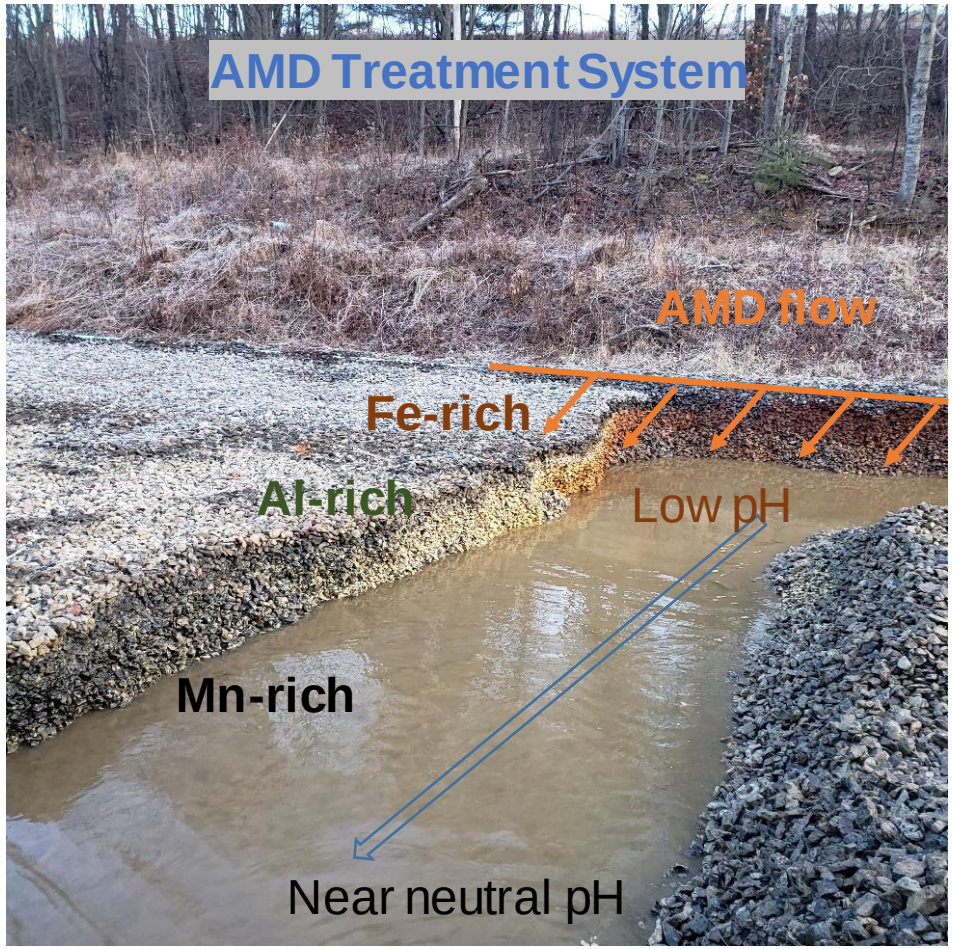


Stuckman et al. (2019), PCC

Acid Mine Drainage (AMD) and Treatment Systems

Appalachian Acid mine drainage with decreased pH, mobilizes metals: Iron (Fe), manganese (Mn), and aluminum (Al), REE, Cobalt and Nickel

1,102 tons / year REO recovery potential (~12% US annual demand)



AMD Remediation Treatment: >200 systems in Pennsylvania, USA

Limestone beds to raise pH of water and to precipitate dissolved metals (Fe, Mn, Al)

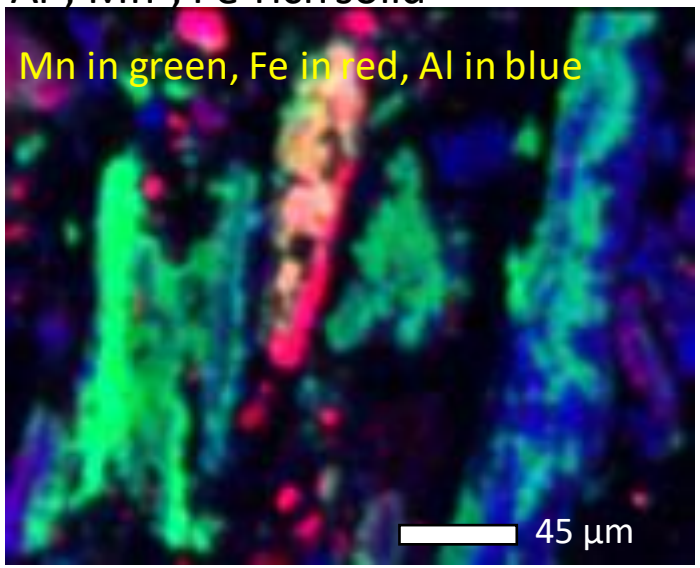
- 90% REE, Cobalt, Nickel co-precipitate with Fe, Mn, Al treatment sludge
- $3 to $400 REE value and $0.04 to $217 Co value/ metric ton dry solid

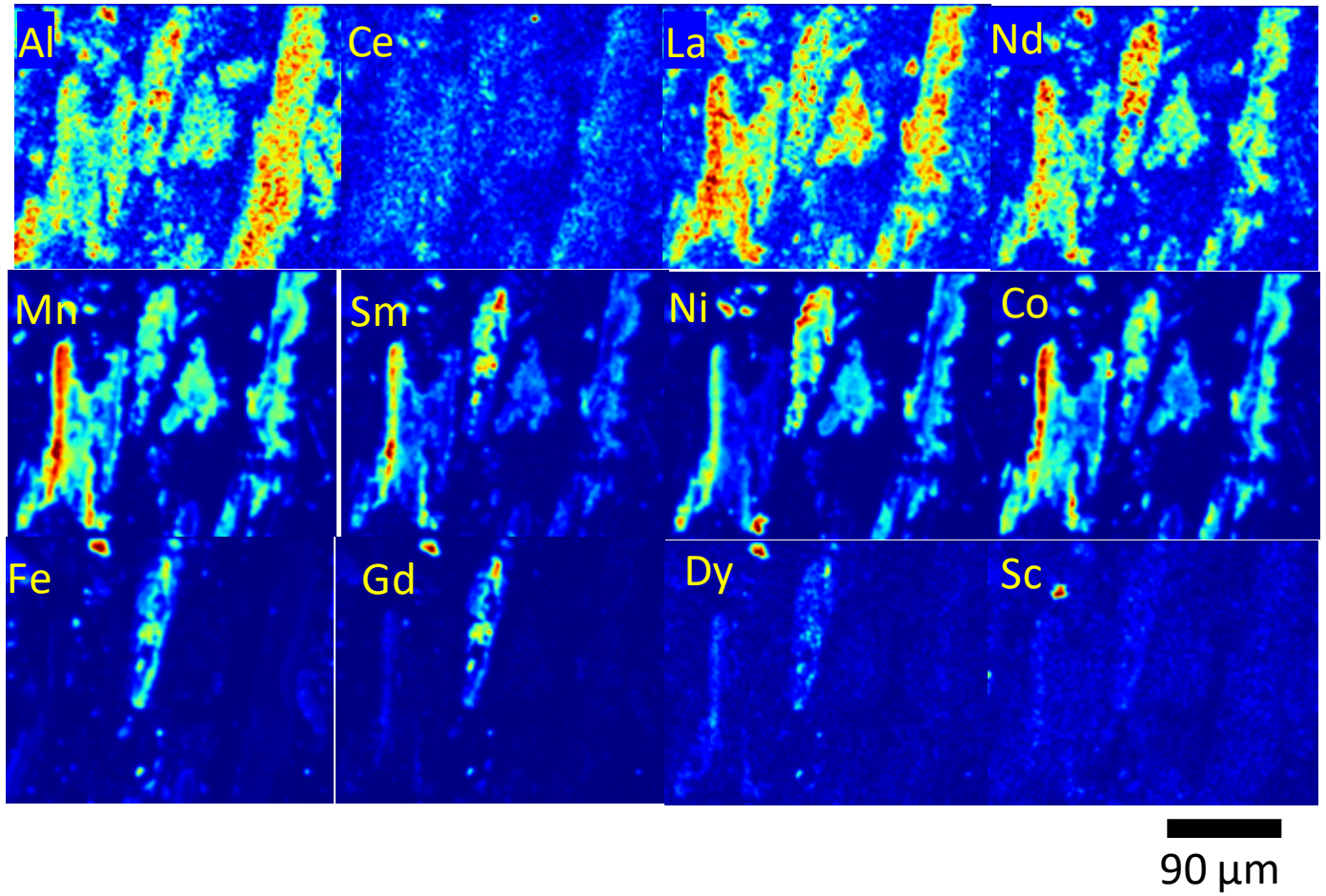
~18,000 tons/year AMD treatment solids

Al, Mn, Fe Rich AMD Solid

- REEs Co-localized with Al and Mn, selected heavy REEs (Gd, Dy) co-localized with Fe
- Co, Ni, Zn co-localized with Mn

Al-, Mn-, Fe-rich solid





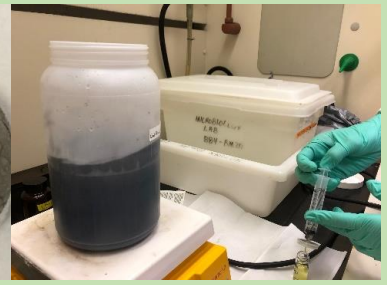
Targeted Rare Earth Extraction (TREE)*

Targeting Calcium-Rich Ashes and AMD solids

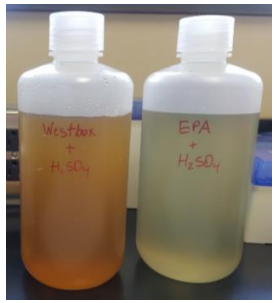
TREE Advantages over REE mining:

1. Domestic/ local waste feedstocks
2. No-pretreatment
3. Up to 90% acid reduction
4. No heating/ no pressure
5. No solvent use or reduced solvent use
6. Less waste management cost
7. Additional value streams such as cobalt, nickel or scandium

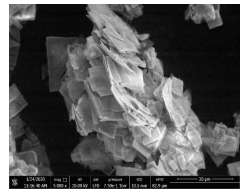




AMD solids Fly ash TREE process



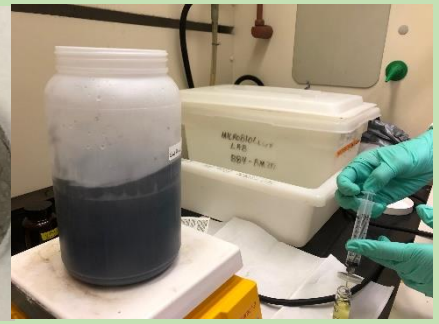
Clean REE leachate



*Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2021) U.S. Patent Pending, Serial No.: 63/053,925 https://netl.doe.gov/node/10318

TREE demonstrated reduced solvent use





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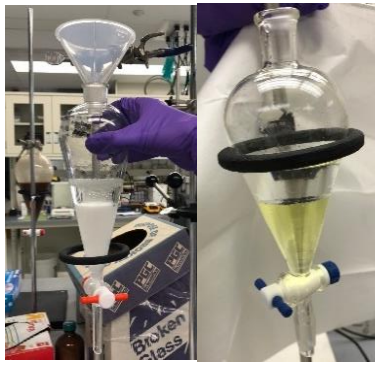
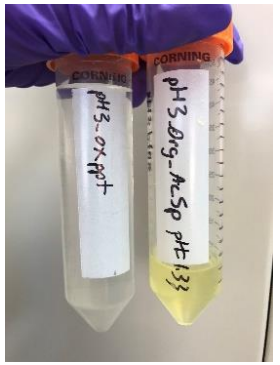
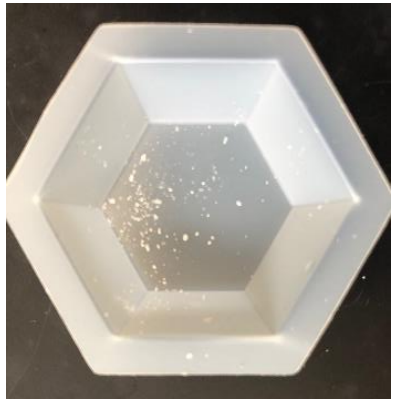
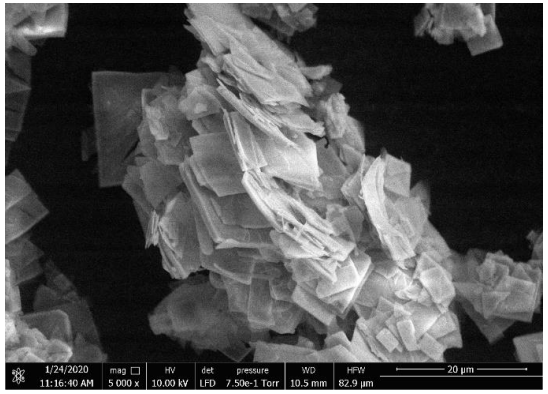


3% solvent used compared to industry



Precipitation

REE Products with up to 96%wt REOs

SEM for pure REE oxalates

TREE Process Scale-Up

Bridging the "Valley of Death" for Cost-Saving and Eco-Friendly REE/CM Extractions

Secretary of Energy's Excellence Award

NATIONAL ENERGY TECHNOLOGY LABORATORY

Scale-up diagram and 50-gallon leaching barrels at NETL

From Bench to Pilot: $1.6 million DOE Technology Commericalization Fund Project together with Wyoming partners committed to technology maturation (University of Wyoming, Coal Valley™ Campbell County, and City of Gillette)

Est. **$140 million to $1.4 billion/yr** in REE/CM value

State, Campbell County pursue rare earth opportunities

By Greg Johnson, Gillette News Record | Via Wyoming News Exchange Jul 5, 2020 Comments OPEN ACCESS

Rare Earth Elements Project Receives Federal Funding

NEWS DIRECTOR | Article Updated: June 23, 2020 | COMMENTS OFF

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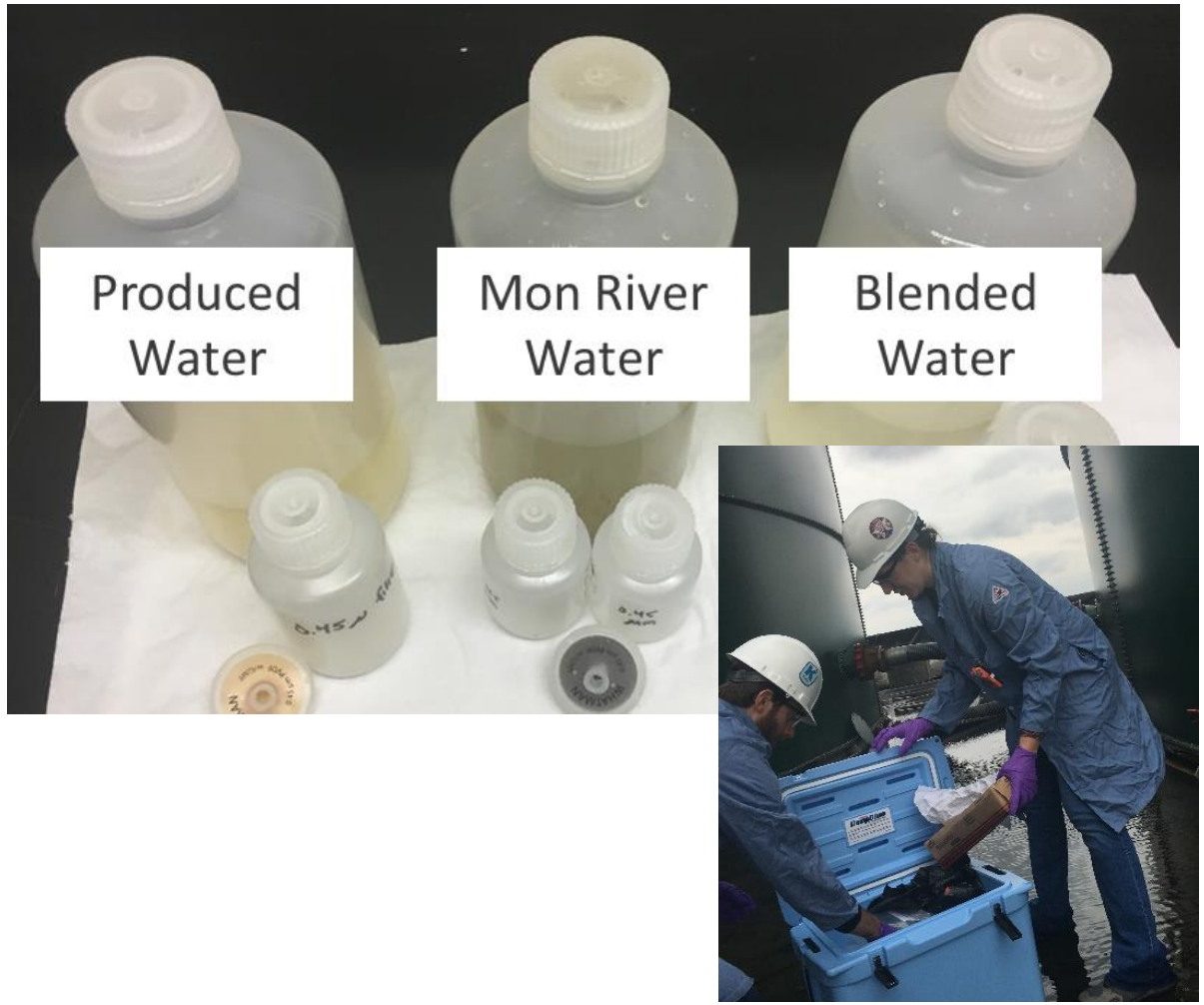
Stay Tuned: Resources from O&G Waste-Water

Extraction of CM from Complicated Brines



Acknowledgement

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Many Thanks to the Team for Their Hard Work During the Pandemic

- Burt Thomas – RIC REE TPL (NETL)
- Brianna O'Neal-Hankle (MLEF-NETL)
- Josh Miller (ORISE-NETL)
- Matt Reeder and Patricia S-V (Leidos-NETL)
- Pittsburgh Analytical LAB (NETL)
- Dr. Sam Webb, Dr. John Bargar, Dr. Adam Jew, Dr. Nick Edwards, Dr. Sharon Bone (SLAC)
- The synchrotron work was conducted on beamlines 2-3, 4-1, 10-2, 7-2 at the Stanford Synchrotron Radiation Lightsource (SSRL), a national user facility operated by Stanford University on behalf of the Department of Energy, Office of Basic Energy Sciences, Office of Biological and Environmental Research and the National Institutes of Health.

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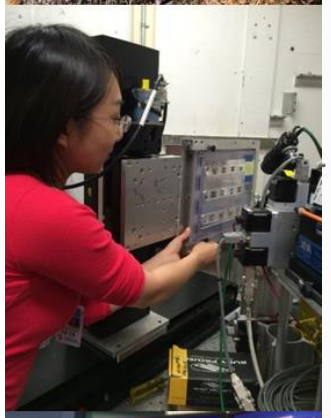
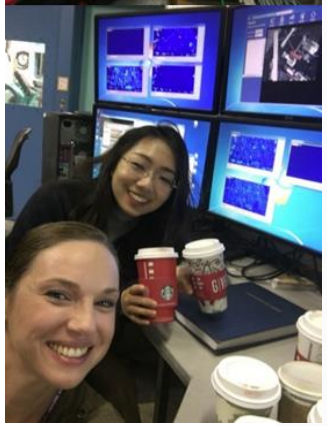
Hope you enjoyed the tour!





Mn in red, Ni in green, Co/Fe in blue

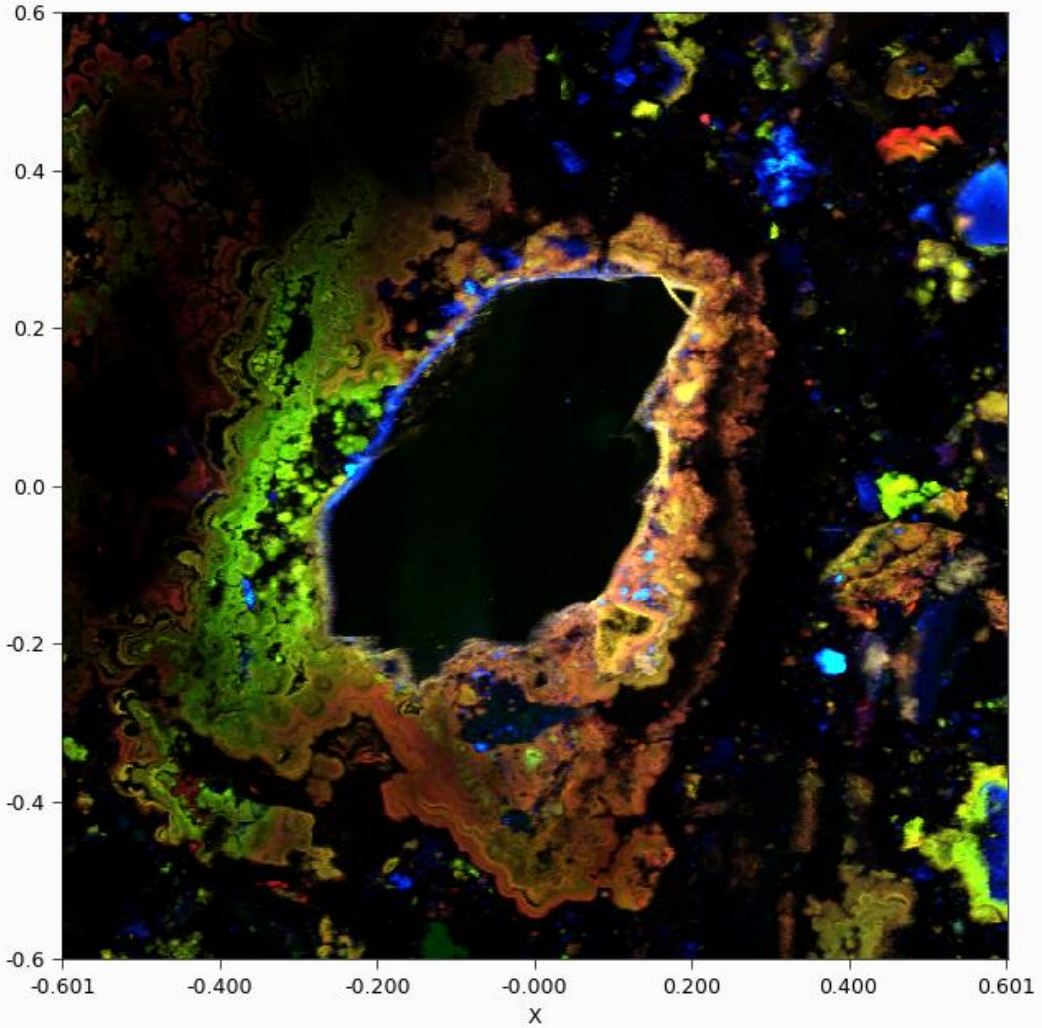


Image 1.2mm x 1.2 mm, 2 μm spot (APS GSECARS, Sector 13)

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