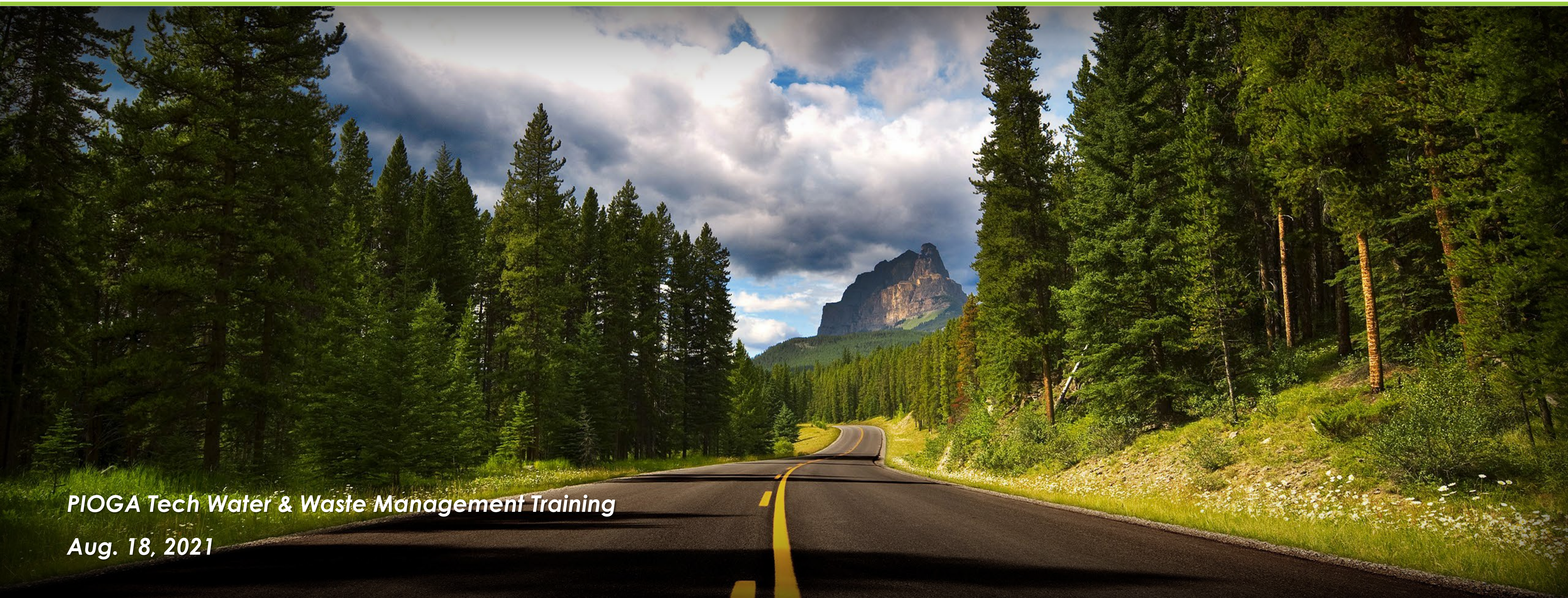
Sustainable Critical Element Recovery Based on Advanced Geochemical Characterization

NATIONAL ENERGY TECHNOLOGY LABORATORY

Mengling Stuckman, Ph.D.

Research and Innovation Center



PIOGA Tech Water & Waste Management Training

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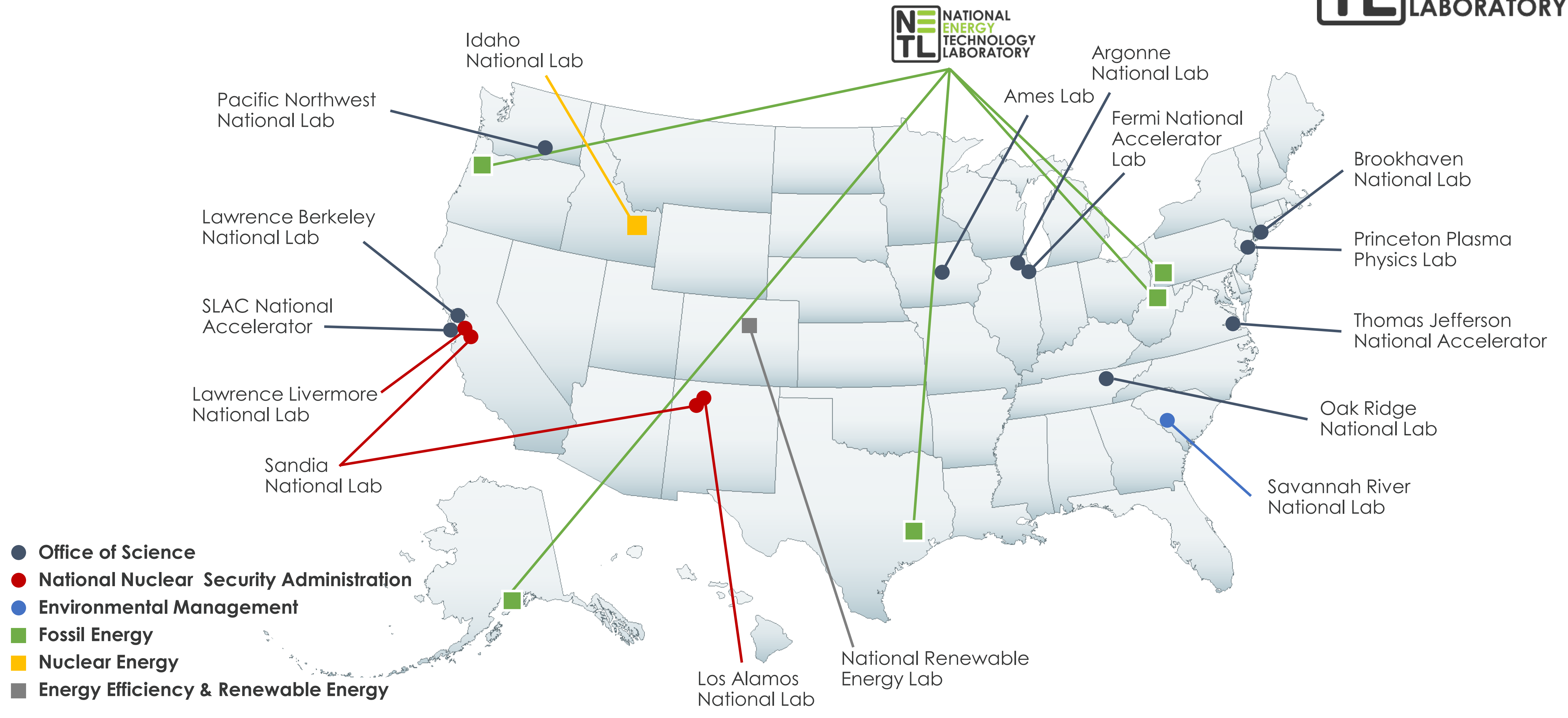


NETL – RIC: Geological and Environmental Systems

Clean energy production from fossil energy sources by focusing on the behavior of natural systems at both the Earth's surface and subsurface, including prediction, control, and monitoring of fluid flow in porous and fractured media

Core Capabilities:

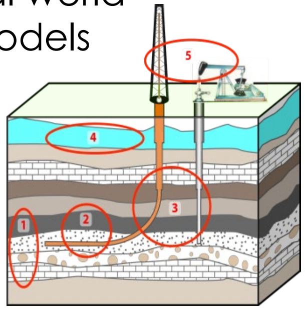
- Multiscale Assessments
- Multiphase Fluid Flow
- Geomaterials (physical and chemical aspects of earth materials)
- Strategic Monitoring of Natural System Behavior
- Geospatial Data Management & Assessment

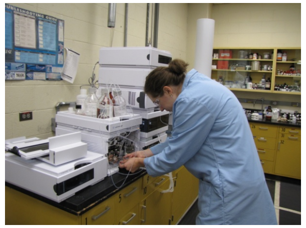
Field

- Applied testing
- baseline monitoring
- data to verify predictions

Computational

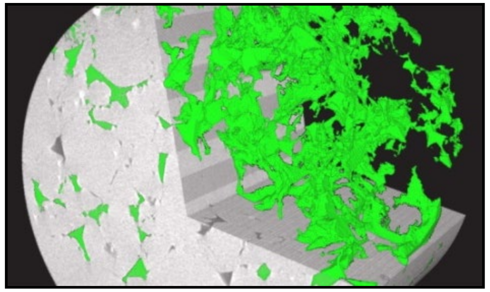
- multiphase flow porous/fractured media
- application to real world
- reduced-order models
- systems models
- GIS/energy datawarehouse





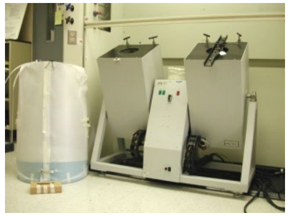
Analytical

- fluid analysis (metals; organics; isotopes)
- solid analysis (EMs, XRD, CT, XRF)



Experimental

- fluid-solid reactions
- high PT
- long-term, larger scale



https://www.netl.doe.gov/research/on-site-research/research-portfolio/geological-environmental-sciences

Research Interests

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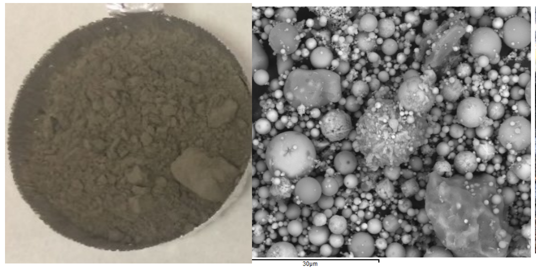
Sustainability of Energy Systems via Advanced Characterization

1. Effective recovery of rare earth elements and critical minerals (REE/CM) from coal byproducts: Ash materials, underclay, acid mine drainage (AMD)

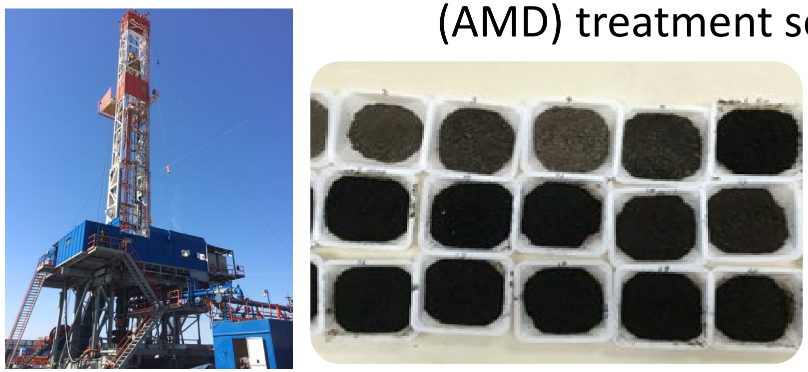
2. Waste management for drill cuttings from shale gas extraction – Factors controlling metal release that impact environments

3. Trace Metal Point Sources – Produced water chemistry (e.g., Li) & environmental impacts of CO_2 storage and energy systems



Coal Ash

Acid mine drainage (AMD) treatment solids



Drill Cuttings from Hydraulic Fracturing

Produced waters from enhanced oil recovery (EOR) fields

Critical Mineral

35 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 FE Feedstocks
Aluminum	China	Canada	Aircraft, power transmission lines, alloys	AMD solids, fly ash
Barite	China	China	Oil & Gas extractions, Lead-acid batteries,	Drill cuttings
Cobalt	Congo	Norway	Jet engines, rechargeable batteries	AMD solids, drill cuttings
Lithium	Australia	Chile	Rechargeable batteries, Al-Li alloys for aerospace	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

Research Approach

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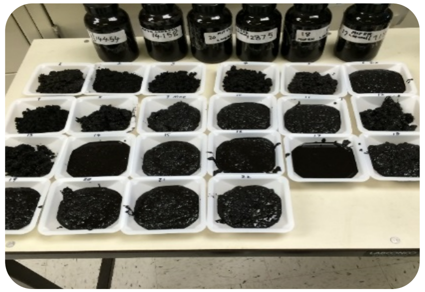
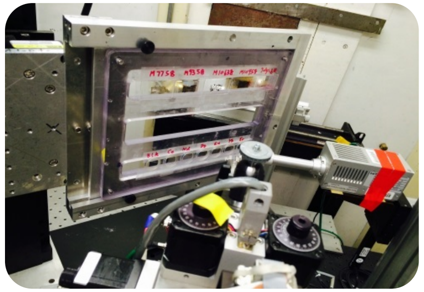
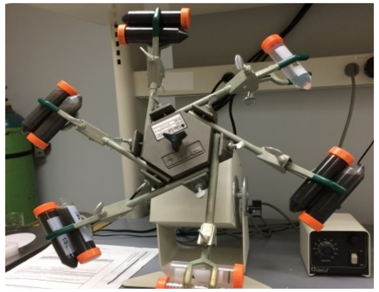
Targeted Solutions Based on Traditional and Advanced Characterizations







Bulk Solid Characterization

- Elemental Composition: ICP-MS, C and S content

-Mineralogy: XRD

Elemental Distribution and Mobility

- **Synchrotron** micro-analysis

- SEM

- **Sequential extraction**

Targeted Leaching

- pH titration

- Redox: Wet vs. Dry, reducing agents

- Short- vs. long-term

Sustainable solutions

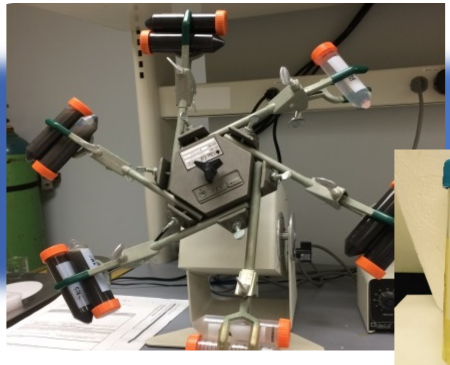
- Identify beneficial use potential (types of CM, or feedstocks)
- Explore selective extraction of CMs (Proprietary information)

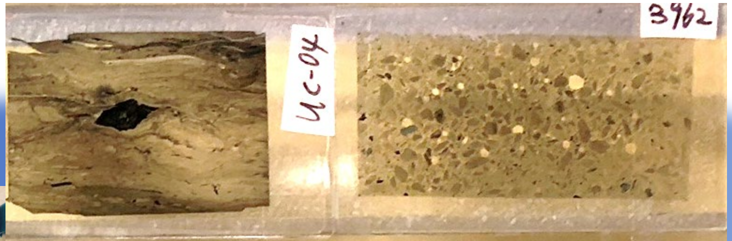
Study 1: Targeted REE and Co, Ni, Zn recovery

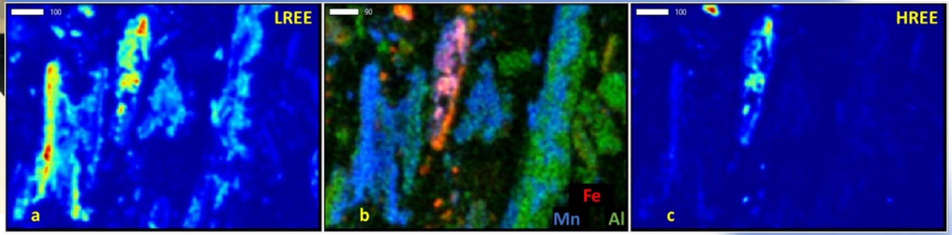
Ash & AMD Characterization to Recovery


AMD solids


Fly ash

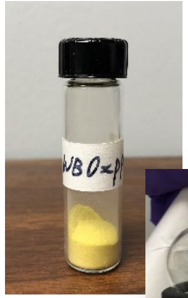


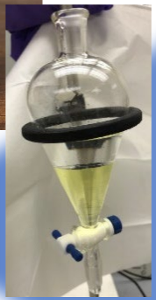


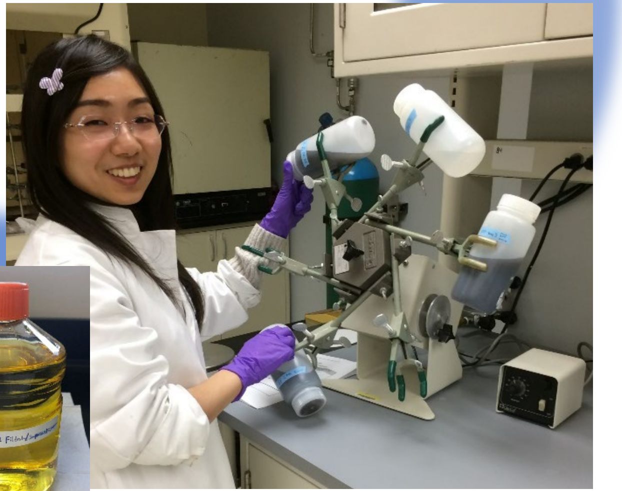


Utilize sequential extraction techniques to **characterize** major REE-hosting solid fractions in different CCBs and to **innovate targeted extractions** for efficient and economical REE recovery.

- A workflow to identify REE & CM host phases & binding environment
- Bulk Chem, Titrations, Sequential Extractions
- Advanced Characterization & Identify targets and Lixiviant
- Selective Extraction Processes Optimize Extraction Efficiency

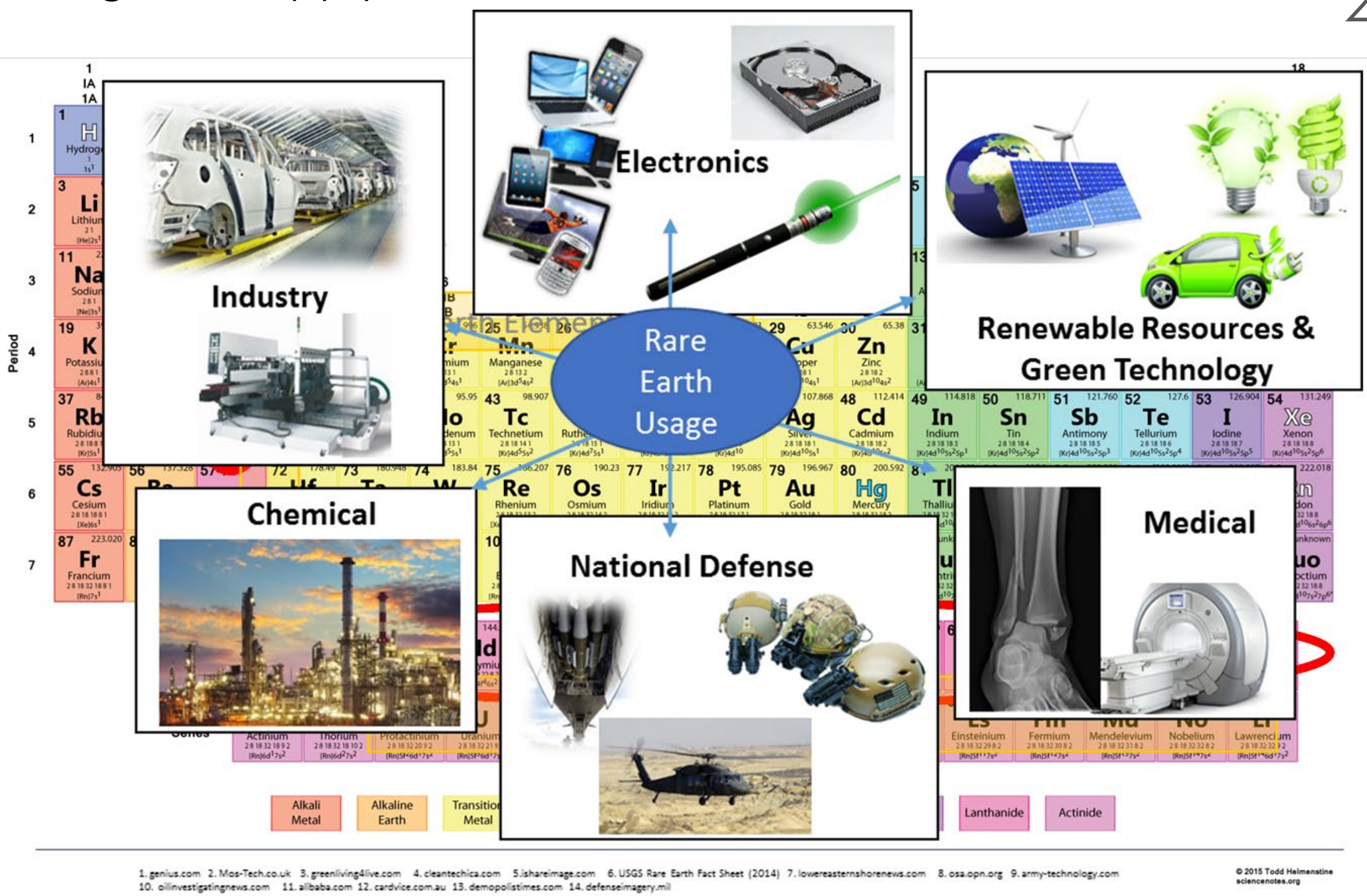






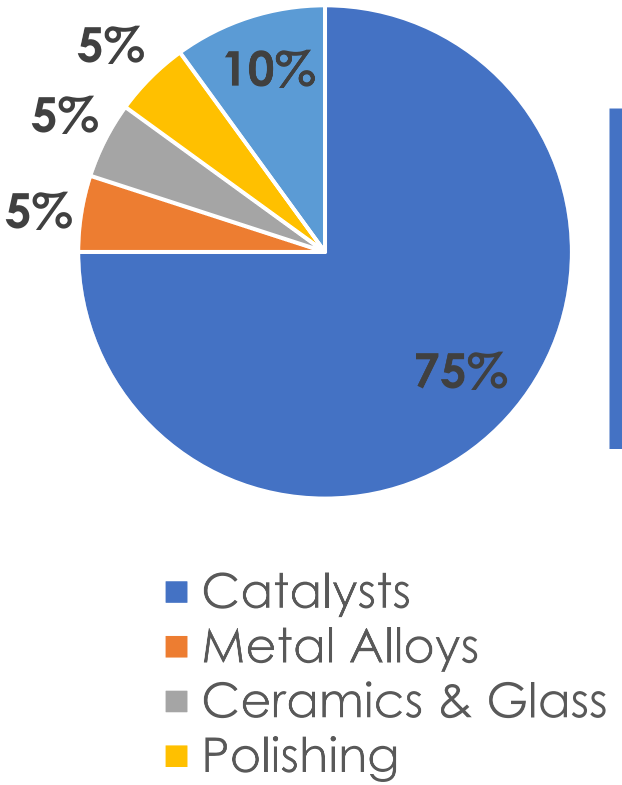
Domestic Rare Earth Element (REE) Use

REE: Sc, Y, 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)
80% global supply from China



Source: USGS

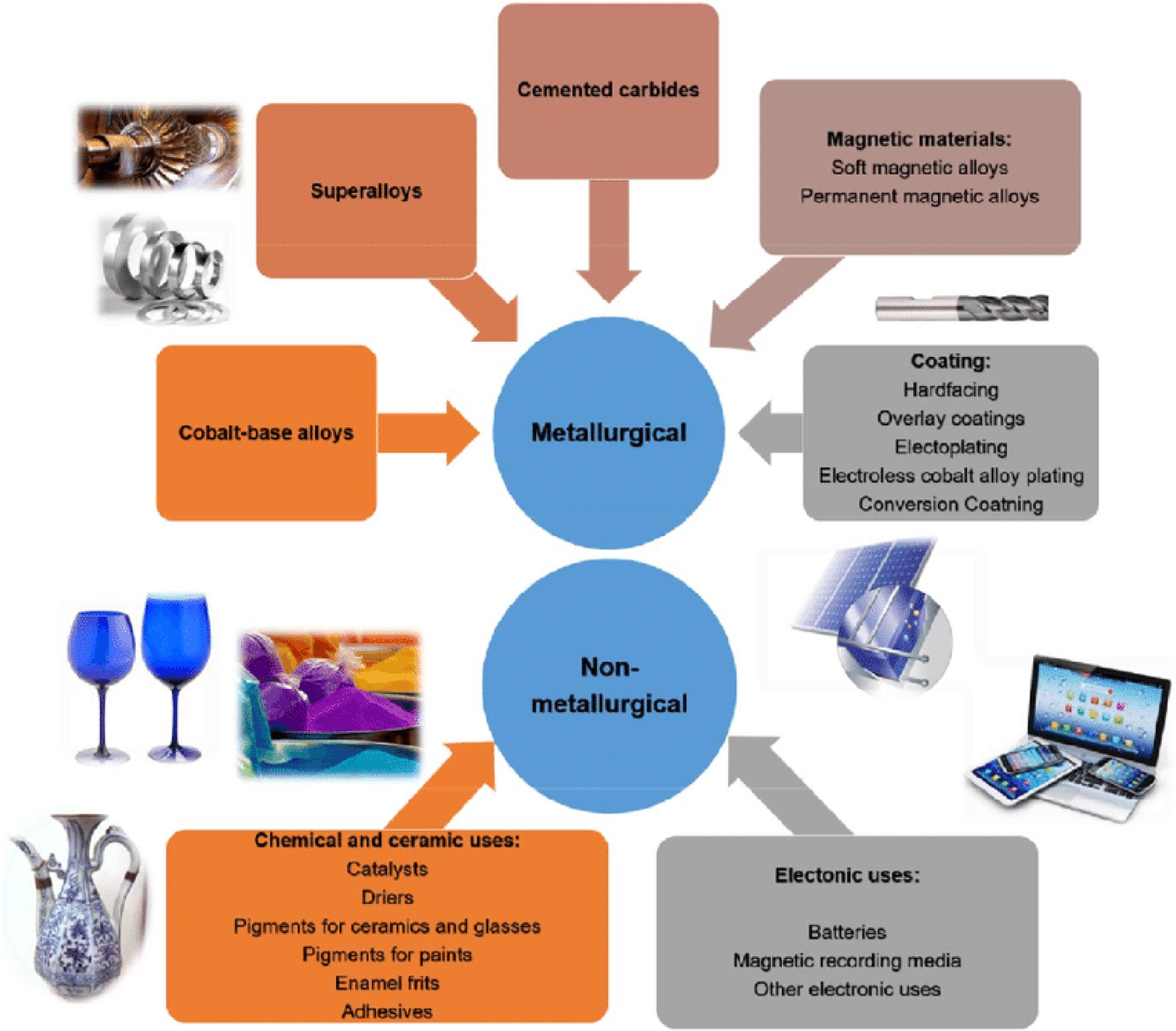
2019 Estimated Domestic End Use for Imported REEs

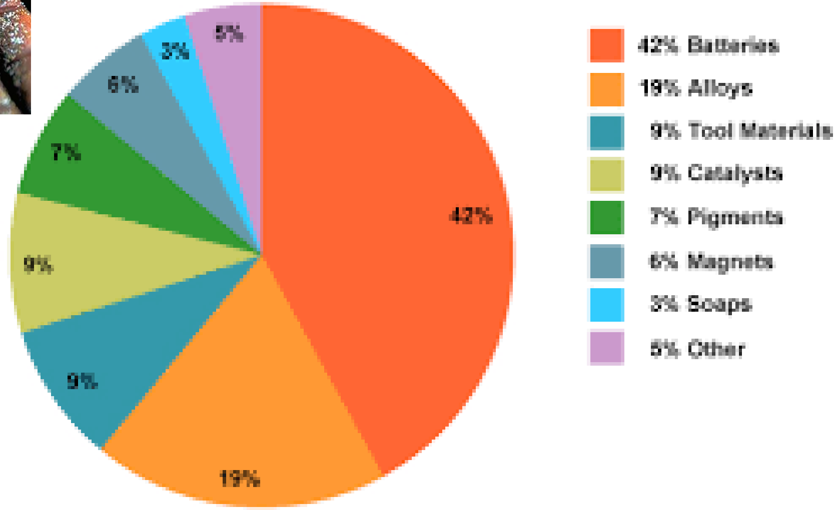


Total U.S Demand for Raw REE Approx. 13,000 mt/year

From Summers et al. (2020) IPCC

Cobalt Use





- Cobalt price comparable to selected rare earth elements
- 50% from Congo, by products from Copper mines

https://www.researchgate.net/publication/326161730_Comparison_of_ion-exchange_resins_for_efficient_cobaltII_removal_from_acidic_streams

Opportunity for Coal-Based 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): est. 8,910 tons REE/yr, 95% of REE demand in 2018[2]**
  - **Acid mine drainage (AMD) in Appalachian basin: est. 500 - 3,400 tons REE/yr., 7% to 41% of REE demand in 2018[3]**
  - Mining underclay and shale

Motivation for advanced characterization:

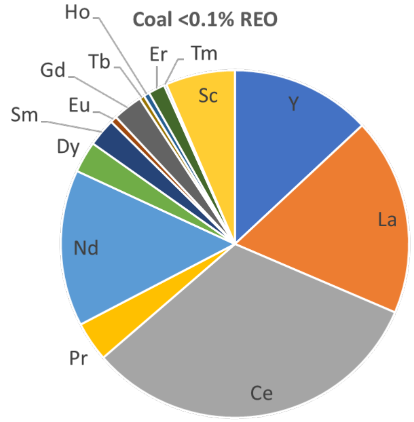
"Differences in radius, oxidation state, and bonding drive fractionation of REEs in natural systems and enable their industrial separation"

Chakhmouradian and Wall (2012)

Goal – Robust Identification of REE speciation in key CCB types

Work Smarter Not Harder

Coal Ash reserve: 113 million tons/yr[1]



AMD solids: 18,000 tons/yr[3]

Key: Little-to-no U, Th

1:Summers et al. (2020) IPCC; 2: Taggert et al. (2018), ES&T; 3. Hedin et al. (2019), IJCG

Acid Mine Drainage (AMD) is Enriched in CM

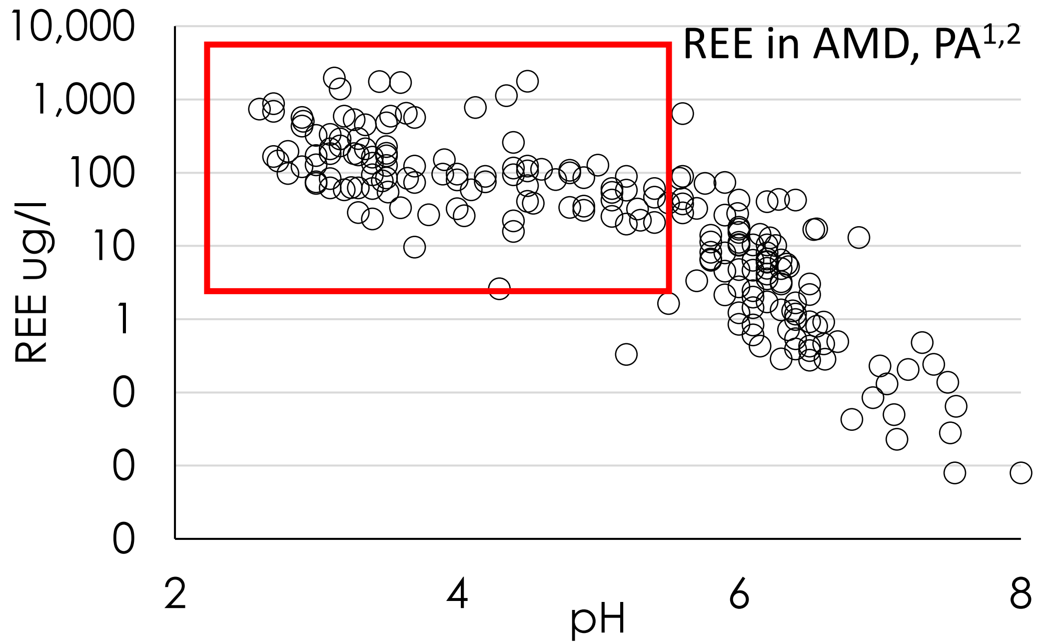
Understanding Rare Earth Element Behavior

Domestic Source of CM

Pyrite (FeS_2) oxidation releases hydrogen ions
- Decreases pH, mobilizes metals (e.g., Fe, Mn, Al)
- Need to treat toxic levels of metals that negatively effect the water, including REE, Co and Ni under acidic conditions

CMs from 140 discharges across Pennsylvania[2]

Element	Max conc. (ug/L)	Min conc. (ug/L)	Max loading (kg/year)	Min loading (kg/year)
Mg	210,000	3,600	3,541,140	40
Mn	74,000	19	215,522	4.5
Sr	3,600	27	83,321	0.23
Ni	3,200	2.6	10,428	0.3
REE	1,765	0.4	7,364	<0.01
Co	3,100	0.3	6,952	0.1
Cu	190	0.4	2,086	<0.1
Li	390	11.0	4,513	0.2



1: (Hedin et al., 2019; Stewart et al., 2017); 2: (Cravotta, 2008; Cravotta and Brady, 2015)

AMD Treatment Systems and REEs

Passive Remediation Treatment: No chemical added, >200 systems in PA

~85 billion gallons/year AMD treated

~18,000 tons/year treatment solids produced

Raises pH of water (Limestone beds)

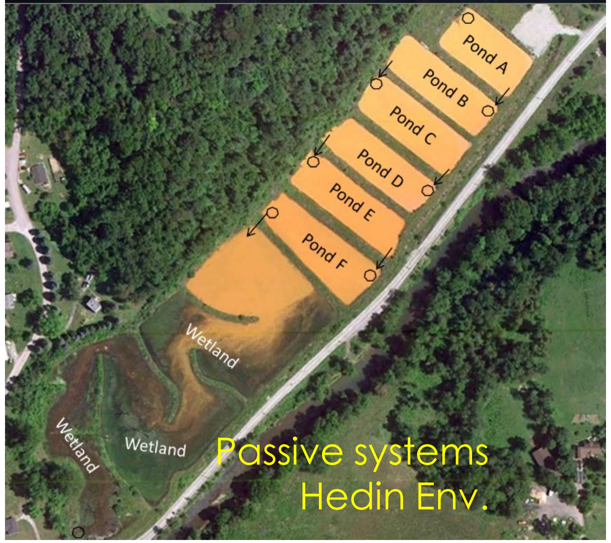
Precipitate dissolved metals

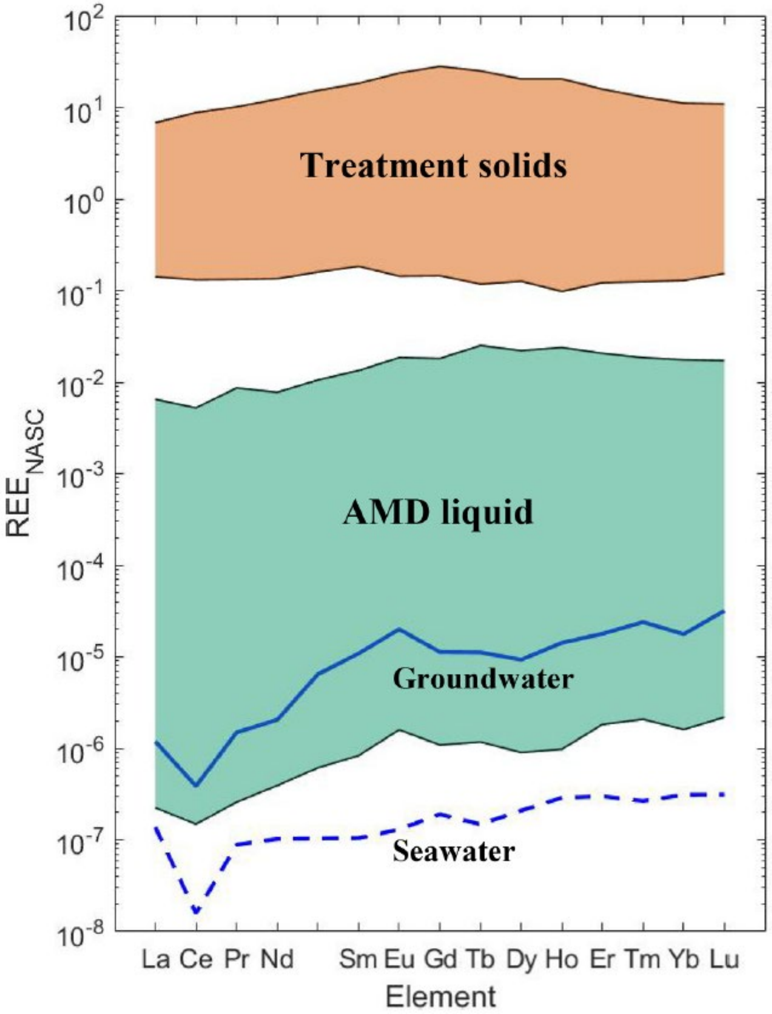
- 90% REE sequestration REE's precipitate with Fe, Mn, Al

Waste solids (metal oxides/hydroxides)

Underground disposal

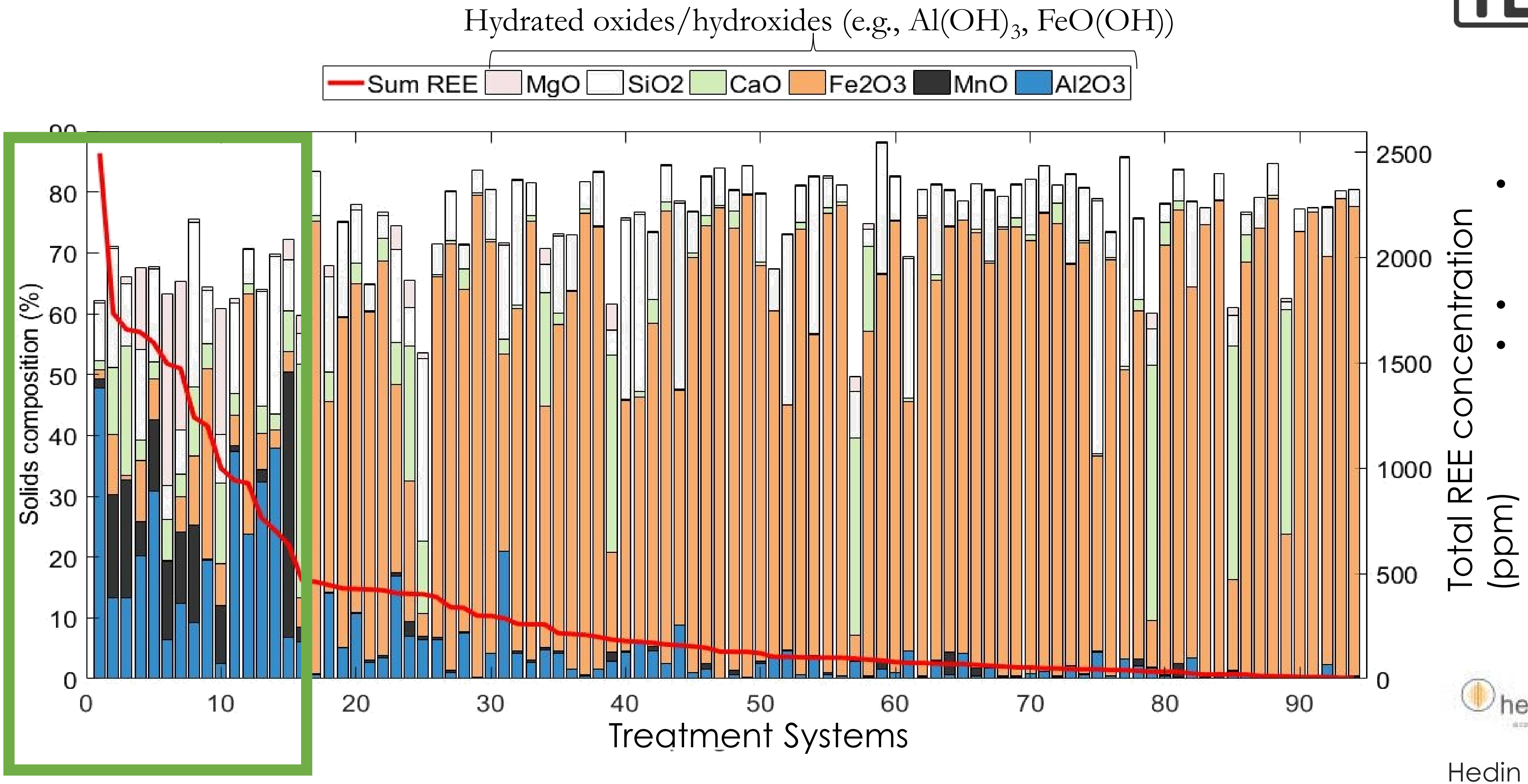
Landfilled





Hedin et al. (2019 & 2020), IJCG

Available ~100 AMD Solids in PA



- ~50% critical REE (Eu, Nd, Tb, Dy and Y)
- <50 ppm U, Th
- $3 to $400 REE value and $0.04 to $217 Co value/ metric ton dry solid

hedinenvironmental

Hedin et al., IJCG, 2020

In-House Analysis for Selected AMD Solids

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Unit: wt% for Major elements and mg/kg for trace elements

	C	S	Al	Si	Fe	Mn	Mg	Ca	K	Ti	REY	Li	Co	Ni	Cu	Zn	Sr	Ba
Al rich solid	2%	2%	**18.0%**	19.3%	2.1%	0.1%	0.2%	1.2%	0.7%	0.3%	**1113**	38	22	50	106	315	133	216
MnCa rich solid	4%	ND	3.5%	6.1%	0.5%	**18.1%**	0.6%	16.8%	0.4%	0.1%	**1590**	108	6026	8889	89	13585	212	151
AlMnFe rich solid	1%	1%	**15.4%**	9.7%	**5.2%**	**8.5%**	0.2%	2.8%	0.3%	0.1%	**1900**	440	2059	3002	518	5812	53	100

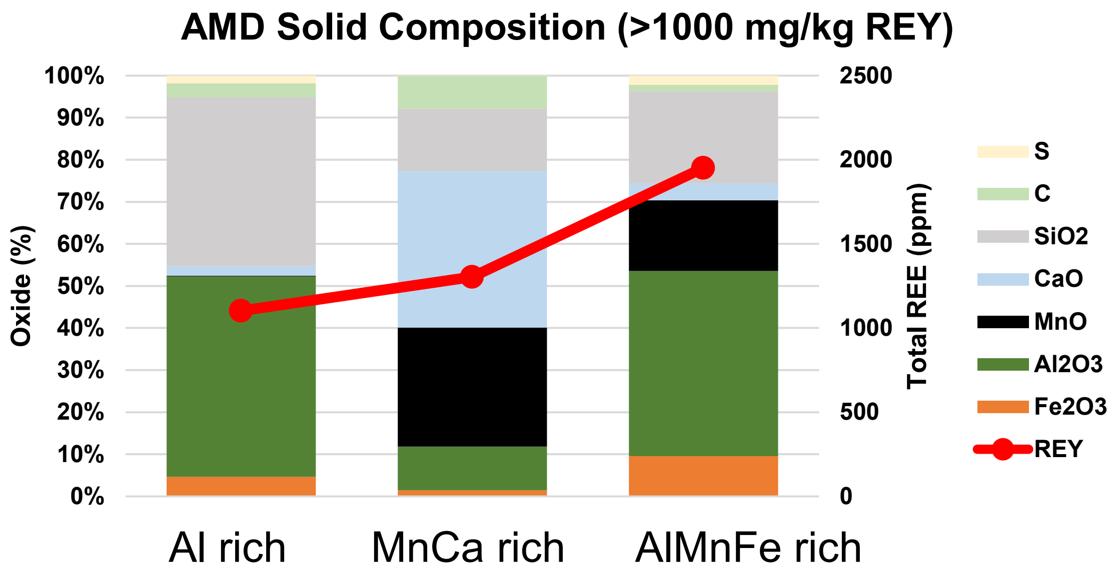
The transition metal contents are sometimes higher than REY; Lithium content is also reasonably high

MnCa-rich solid has higher accumulation of Co, Ni and Zn

Al-rich solids

MnCa-rich solid

Al-, Mn-, Fe-rich solid



Hedin et al., IJCG, 2019

Where are the REE? Synchrotron Micro-Analysis

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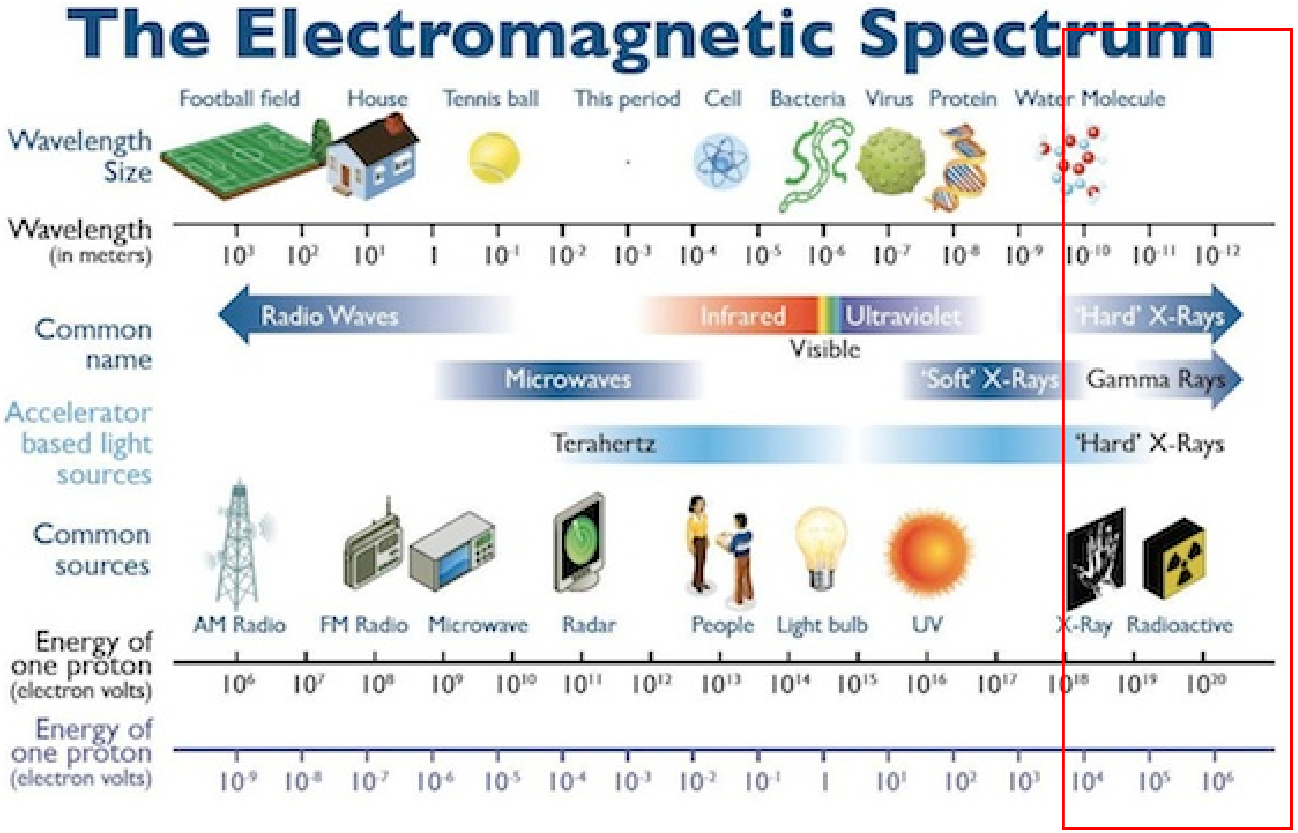
Stanford Synchrotron Radiation Lightsource



>7keV
Elements:
Z>26 (Fe)

Why synchrotron?

Bright beam: 10 billion times brighter than a hospital X-ray

High energy and finely tunable: probing atomic and molecule interactions

Synchrotron Microscopy & Spectroscopy

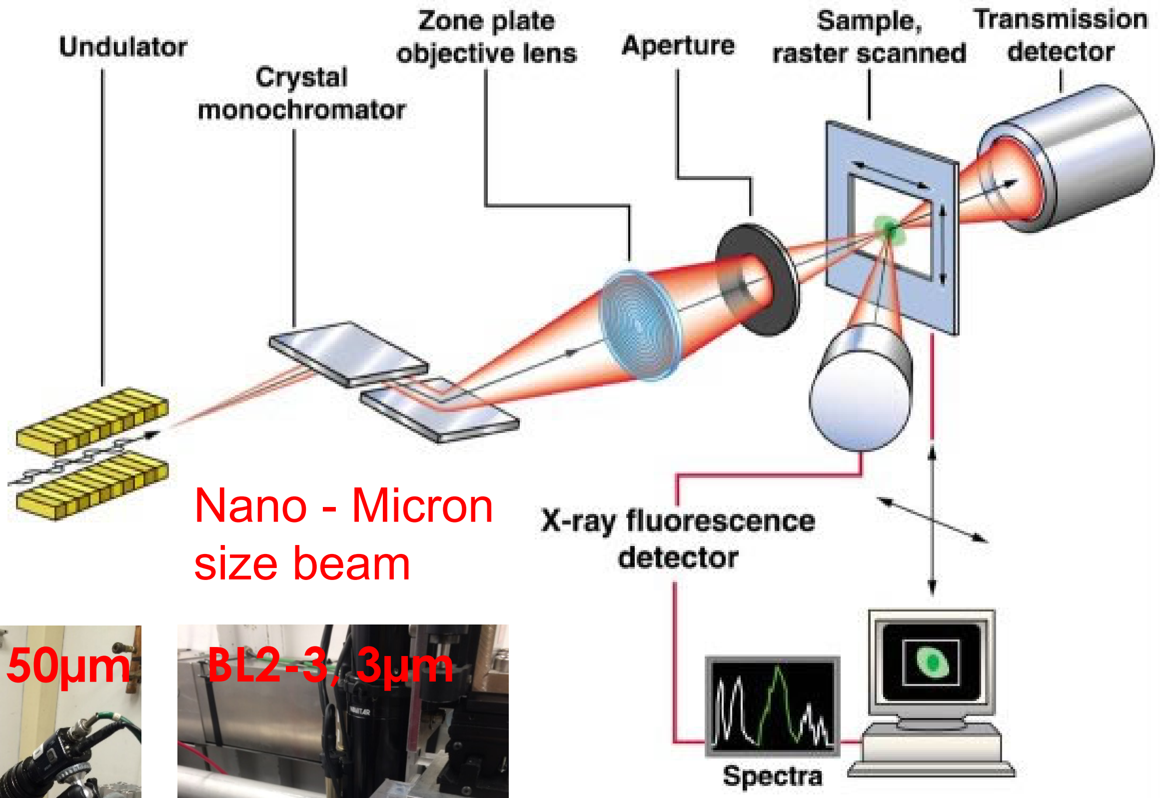
Overall Goal: To Interrogate Binding Environment of Elements of Interest

X-ray Fluorescence (XRF) Microprobe

- Elemental Mapping (aka Where?)
- Fix excitation energy, scan dimension/location

X-ray Absorption Near Edge Structure (XANES)

- Oxidation state, nearest neighbors
- Fix location, scan in energy (around absorption edge of interest)



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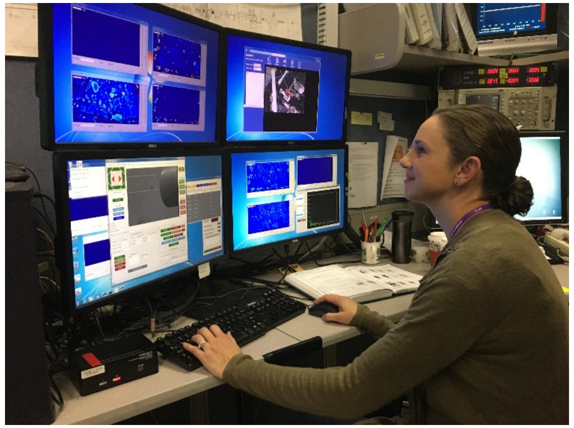
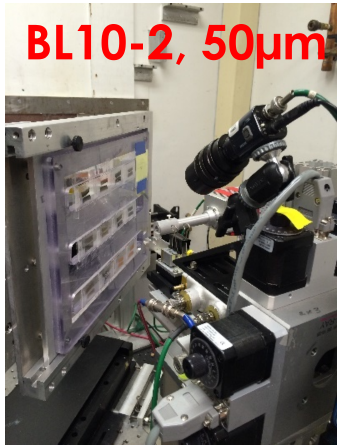
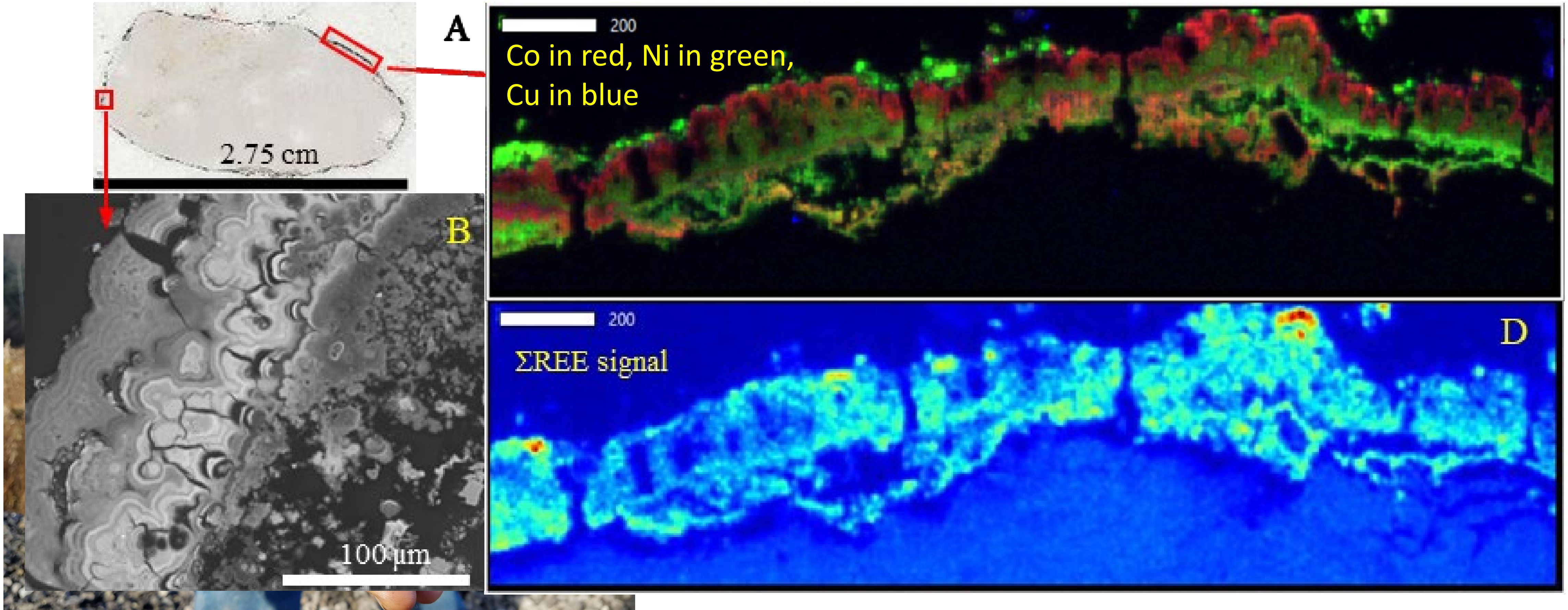




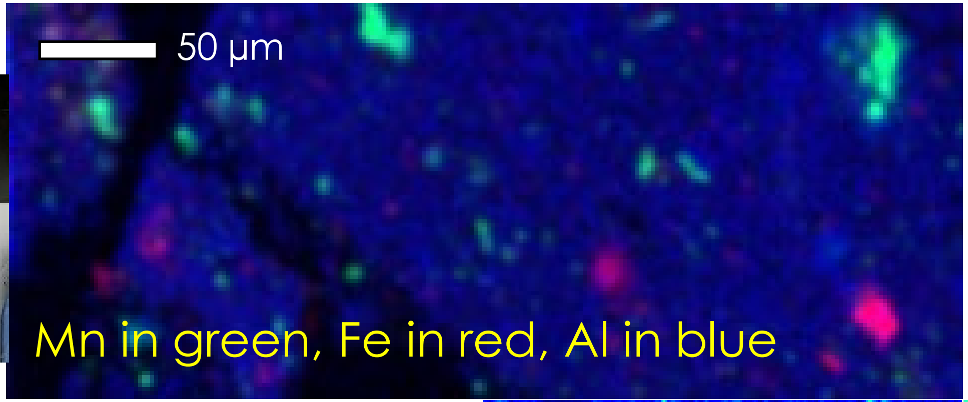
Where are the REE and CM in MnCa Solid?

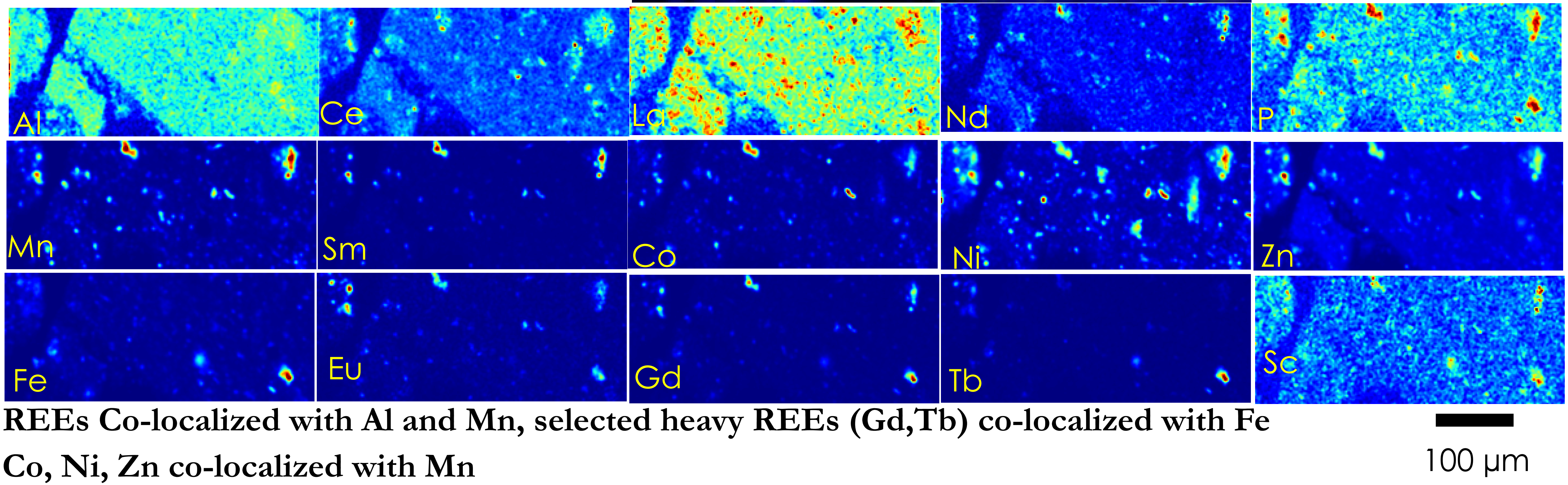
Synchrotron µXRF



- REE associated with Mn layer in CaMn rich solid

Al Rich Solid





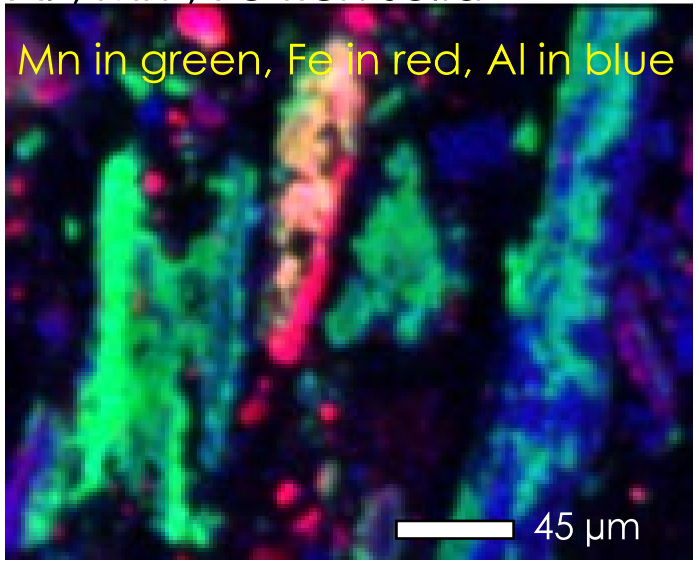
REEs Co-localized with Al and Mn, selected heavy REEs (Gd,Tb) co-localized with Fe

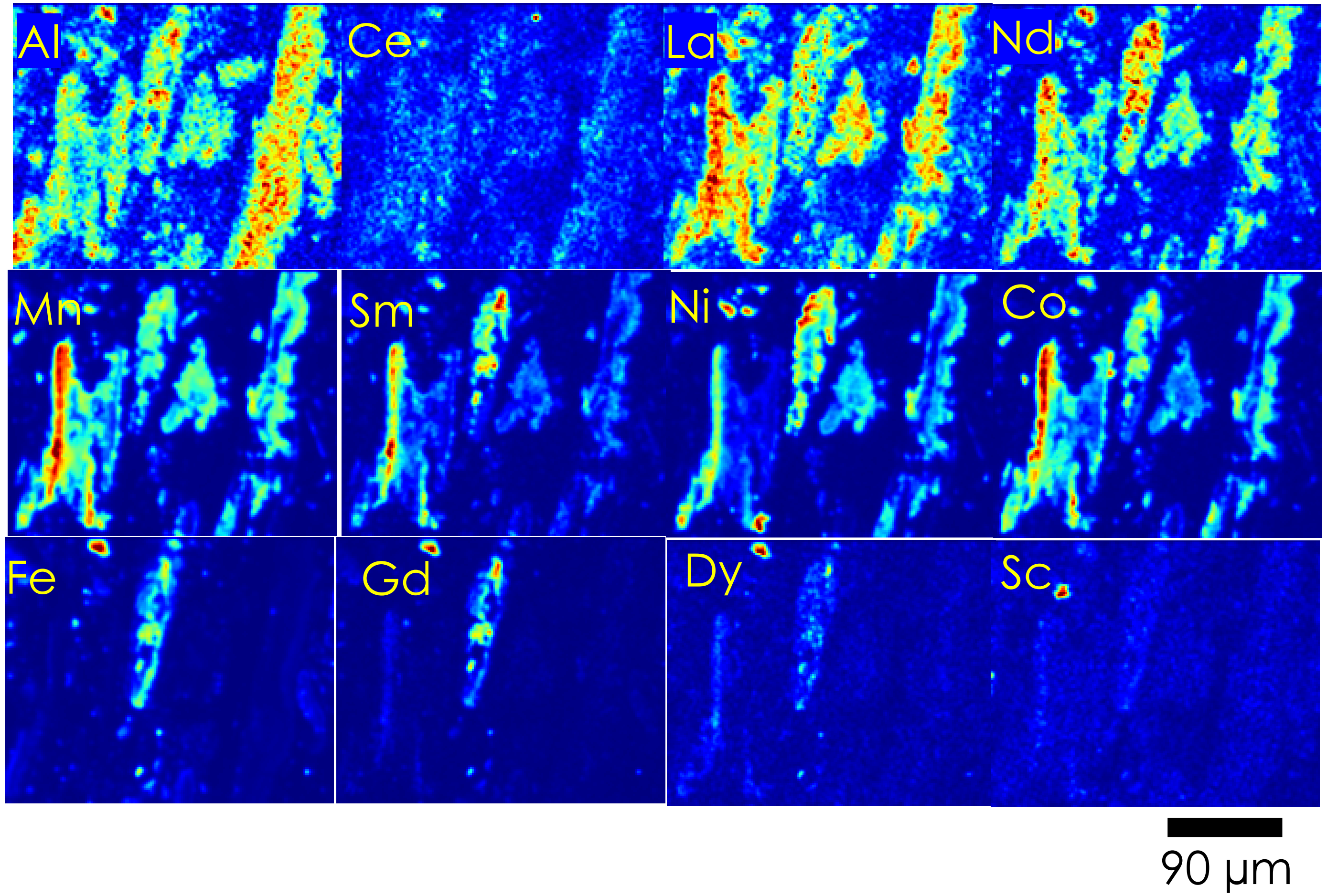
Co, Ni, Zn co-localized with Mn

Al,Mn,Fe Rich Solid

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

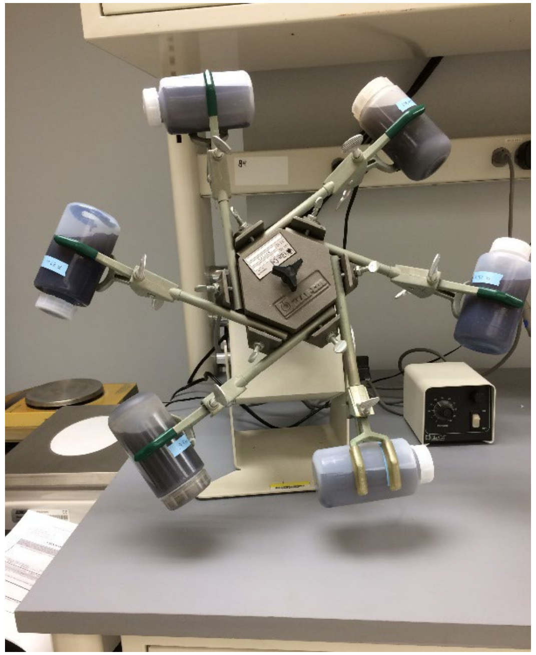
Al-, Mn-, Fe-rich solid





Sequential Extraction Steps (pH Decrease)

Evaluating metal distribution in different solid fractions, originally for soil testing/environmental mobility



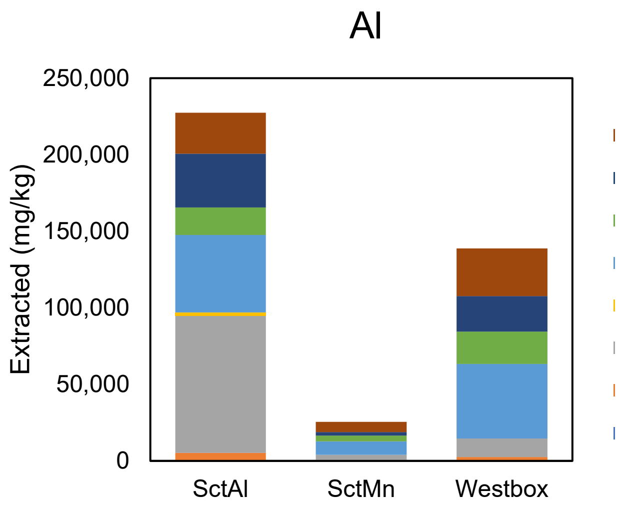
Rotator for extraction @ 30rpm

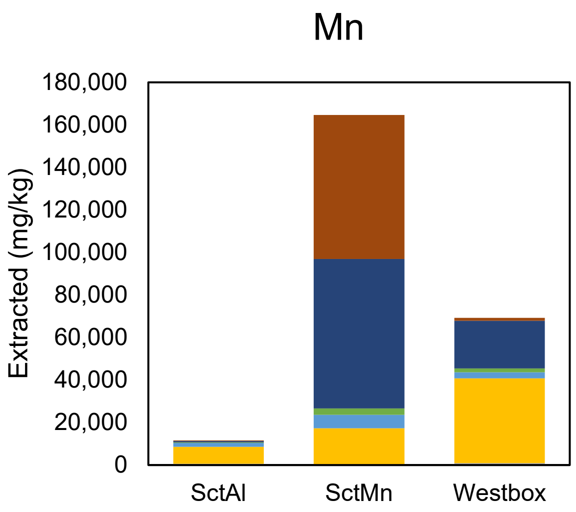
Metal Mobility ↑ / Leachate Strength ↓

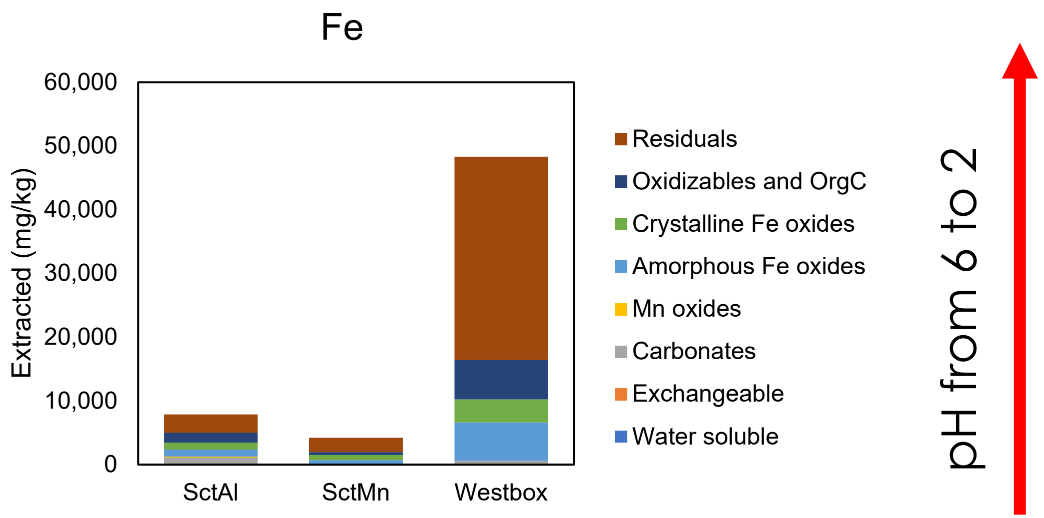
Step #	Targeted Fraction	Reagents	L:S ratio	Temp (°C)	Duration (h)	pH
1	**Water soluble**	distilled water	20:1	25	24	
2	**Exchangeable**	1 M AmAce	20:1	25	24	**6.0**
3	**Carbonate**	1M AmAce	25:1	25	24	**5.0**
4	**Bond to MnO**	0.1 M hydroxylammonium chloride	20:1	25	0.5	**3.5**
5	**Bond to Amorph FeO**	0.2 M ammonium oxalate + 0.2 M oxalic acid in dark	20:1	25	4 in dark	**3.0**
6	**Bond to Cryst FeO**	0.2 M ammonium oxalate + 0.2 M oxalic acid + 0.1 M ascorbic acid	20:1	80	0.5	**2.3**
7	**Bond to Organics and Oxidizable**	1) acidified 30%H_2O_2 2) acidified 30%H_2O_2 3) 1M ammonium acetate wash	10:1 10:1 50:1	25/85 85 25	1 + 1 1 16	**2-3** **2-3** **2.0**
8	**Residual**	$LiBO_2$ Digestion	-	-	-	-

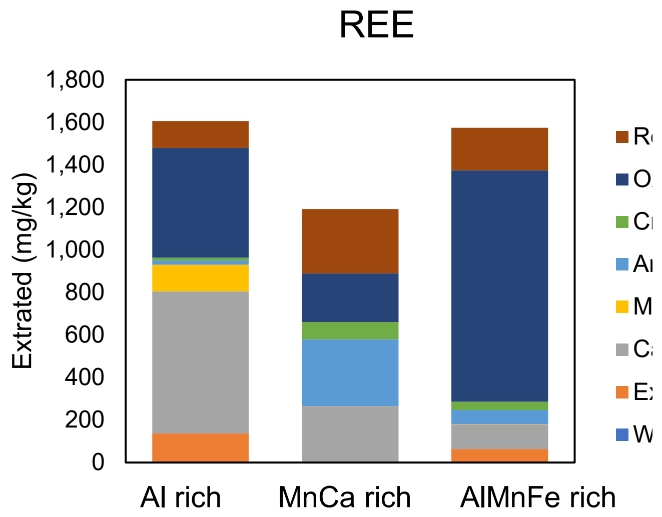
Lin, R., et al. (2018). Fuel **232**: 124-133

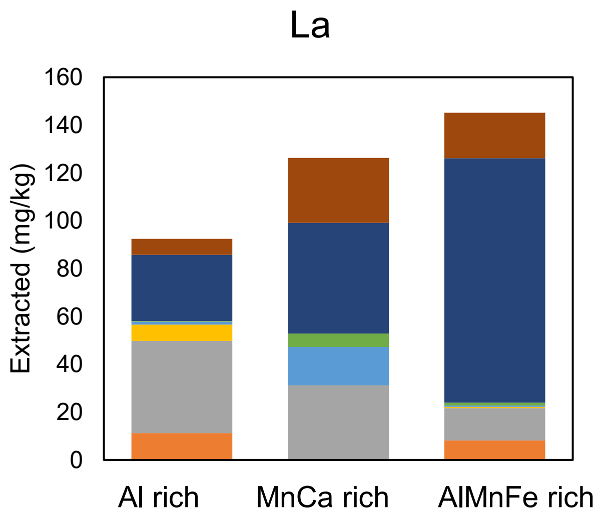
REE Sequential Extractions (Total Exacted vs. Residuals)

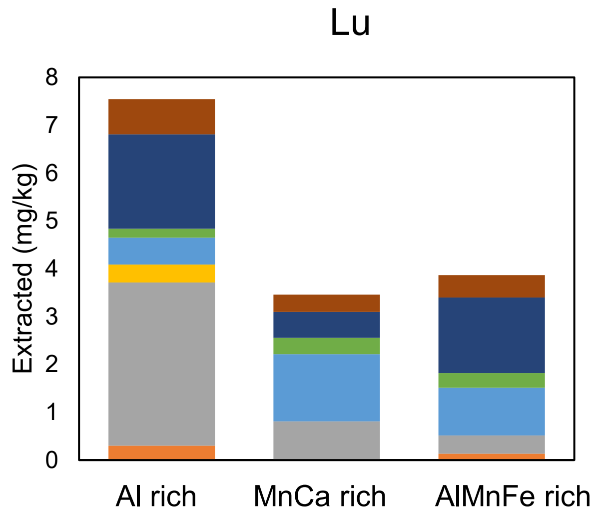












More than 80% REY (Al/Mn) extracted

Heavy REE (Lu) extracted in Amorphous Fe oxides phases compared to LREE (La)

CM Sequential Extractions (Total Exacted vs. Residuals)

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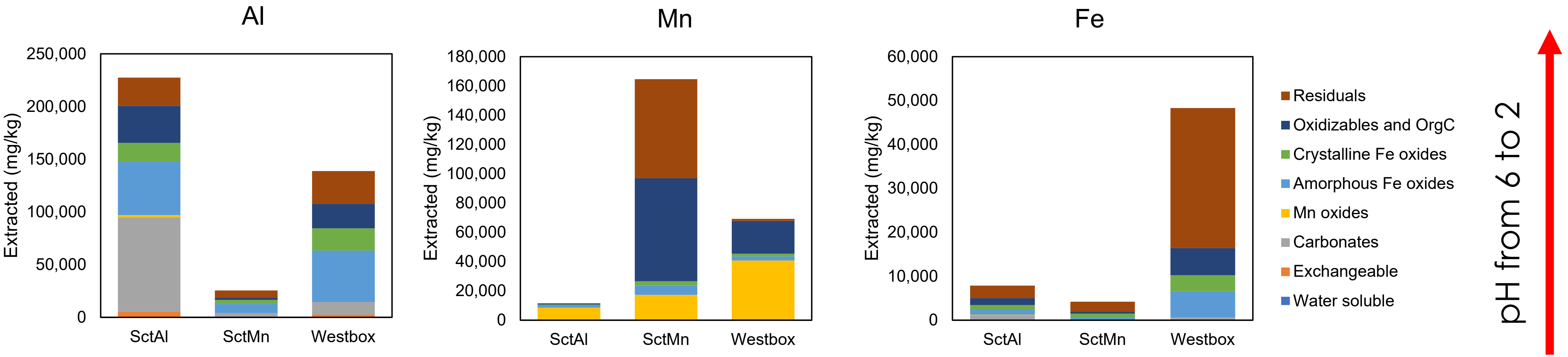

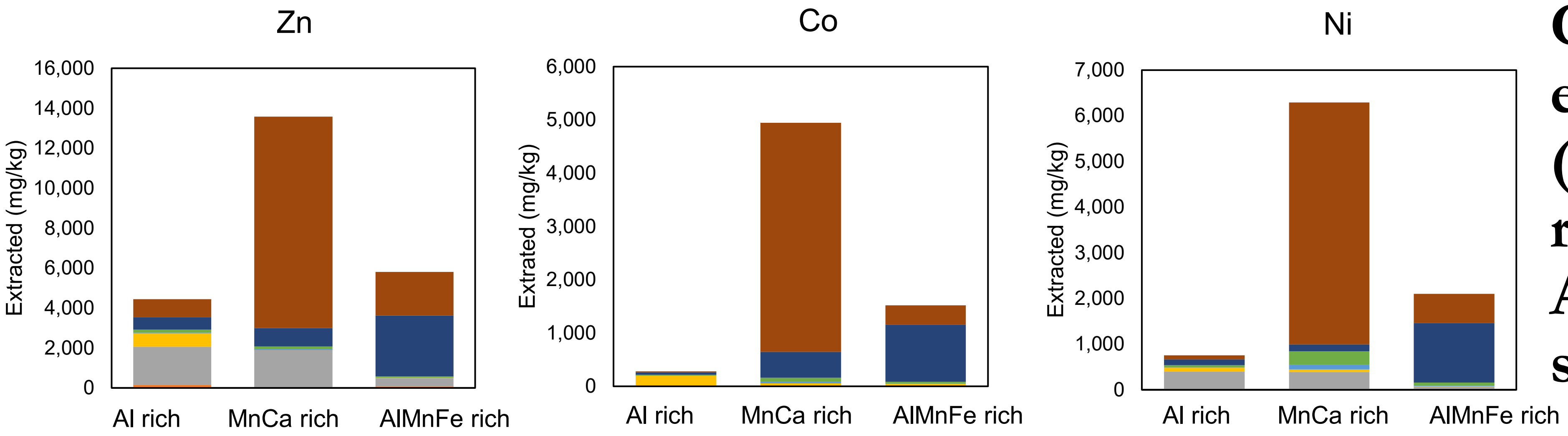

Co, Ni, Zn extractable (>80%) in Al rich and AlMnFe rich solids.

Conclusions

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AMD solids have diverse chemical composition, so extractions may need to be tailored towards different chemical composition.

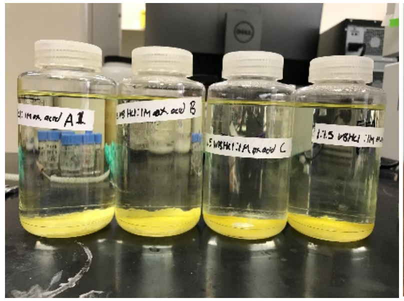
- REEs mostly co-localized with Al and Mn, selected HREEs (Gd/Dy) co-localized with Fe
- Regardless of composition, Co, Ni, Zn mainly co-localized with Mn (hydr)oxides in AMD solids

Innovative Solutions:

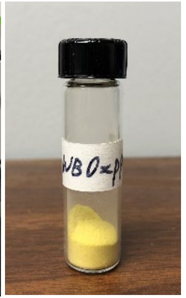
In progress! Novel extractions informed by characterization - Stay tuned for more

AMD solids

Large scale leaching

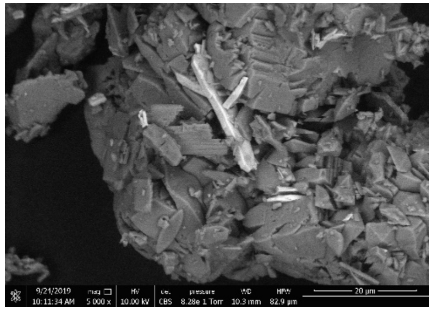


Direct oxalic acid precipitation



Oxalates

13% REE, 48% Zn, 11%Ni, 2%Co



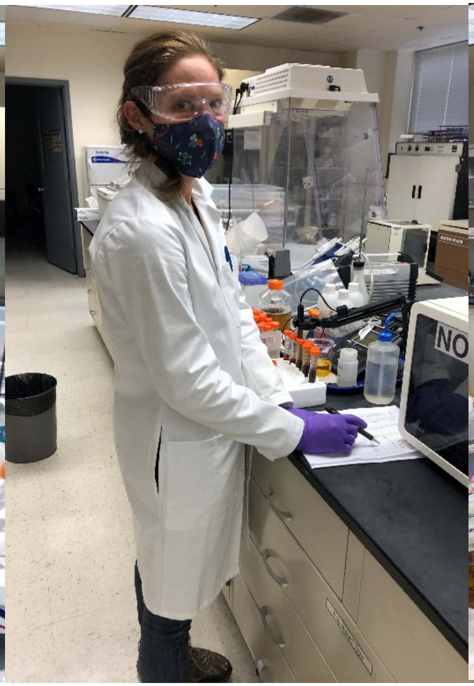
SEM image of REE oxalates in end product

Acknowledgement for AMD work

Many thanks to the team for the hard work during pandemic.

Matt Reeder (LRST)

Patricia S-V (LRST)



Josh Miller (ORISE)

Dr. Ben Hedin (U Pitt)

Research 2: Characterizing CM in Drill Cuttings

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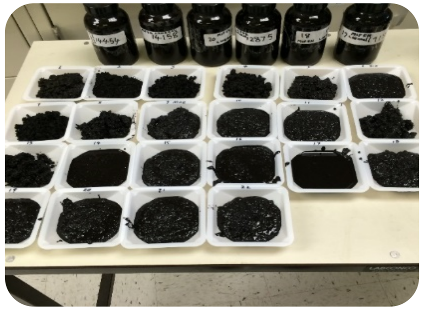
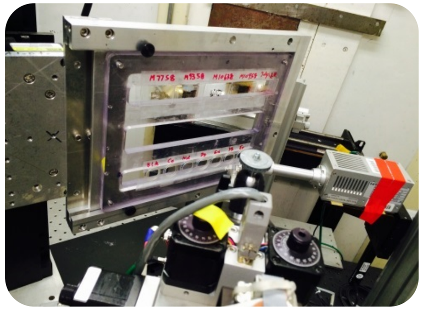
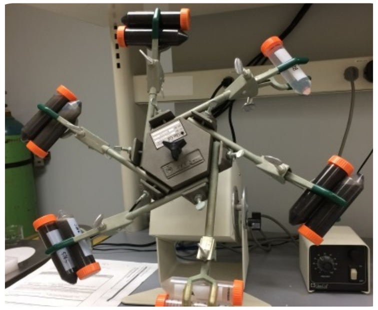
Geochemical Factors Controlling Metal Release in Drill Cuttings from Marcellus Shale Energy Development in order to inform strategies of waste management







Bulk Solid Characterization

- 4 drill cuttings, 2 cores and 1 drilling mud from MSEEL

- Elemental Composition: ICP-MS, C and S content

-Mineralogy: XRD

Elemental Distribution

- Synchrotron micro-XRF mapping

- SEM

- BCR 4-step sequential extraction

Geochemical Leaching

- Regulatory Leaching:

Rain vs. Landfill

- Wet vs. Dry

- pH titration

- Long-term Effect: USEPA 1320 Multiple Extraction

Soil carbon amendment (2021)

- Green-roof soil amendment potential

- Explore selective extraction of CM

Stuckman M.Y., et al. (2019) *Journal of Natural Gas Science and Engineering* 68: 102922.
Stuckman M., et al. (2018), proceeding of Unconventional Resources Technology and Exposition Conference, Houston, TX, 23-25, July 2018

Drill Cuttings from Unconventional Wells

Background

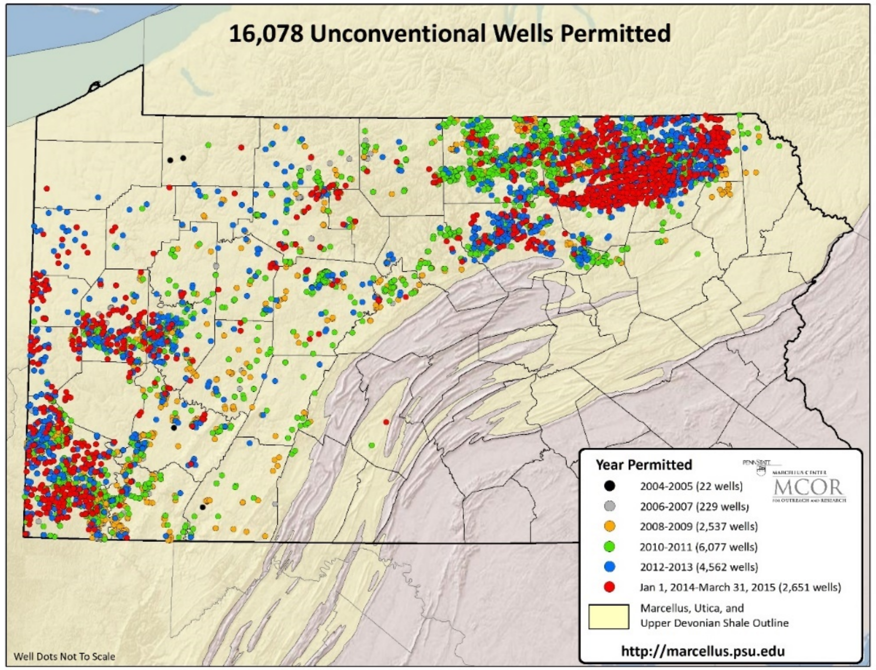


Photo: Drilling site in PA

- From 2004 to March 31, 2015: 16,078 unconventional wells are permitted in Pennsylvania and 9,324 unconventional wells were drilled.
- More than 2,000 tons of drill cuttings are produced from a typical well-drilling operation (per well). In 2020, state records show oil and gas drillers sent 244,000 tons of drill cuttings to landfills.
- Drill cuttings contain both drilling fluids (water-/oil-/synthetic based) and shale rock cuttings

http://www.marcellus.psu.edu/images/PA%20Permit%20Map%202014-1520150331.jpg
Ball et al. , Waste Management Research, (2012)
Fact Sheet - Onsite Burial (Pits, Landfills), http://web.ead.anl.gov/dwm/techdesc/burial/

SAMPLES from Marcellus Shale Energy And Environment Laboratory - MSEEL

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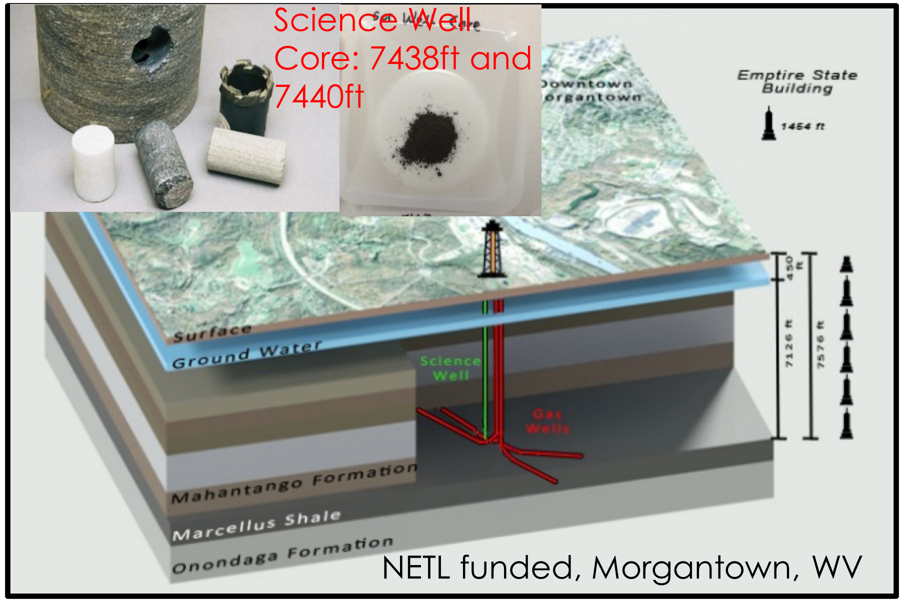
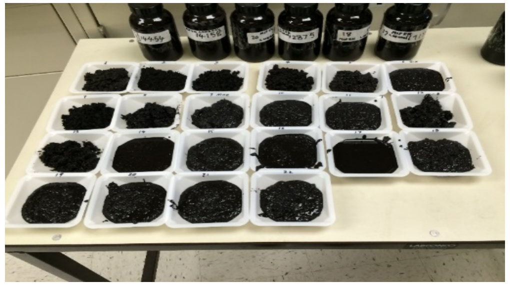
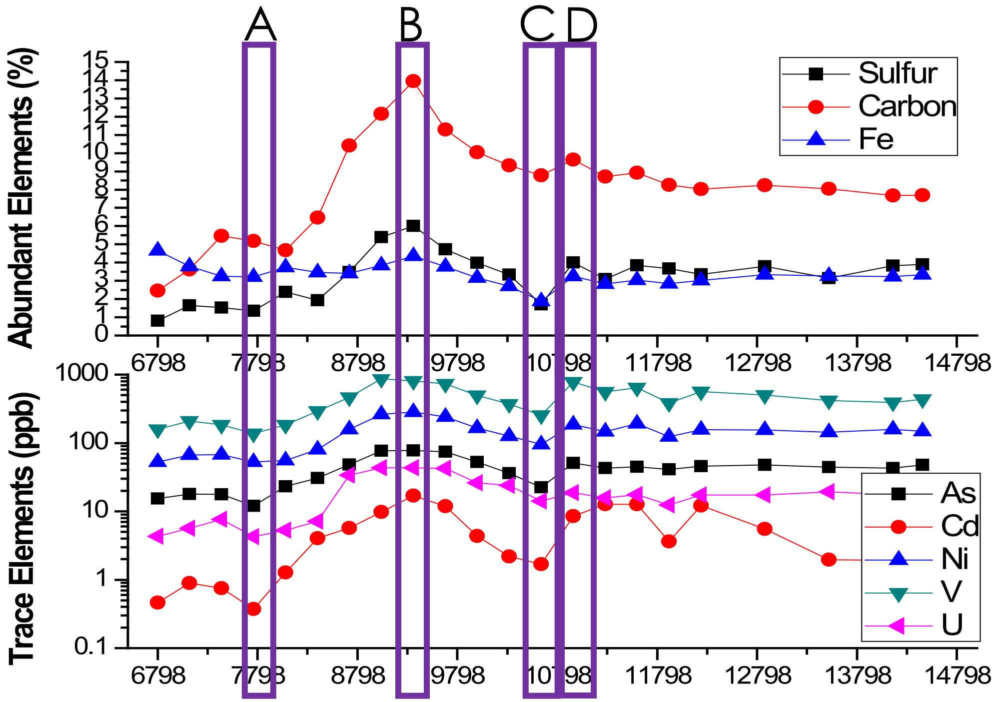
www.mseel.org



22 Drill Cuttings from 5H Production Well horizontally drilled at 7,438ft





49% weight loss

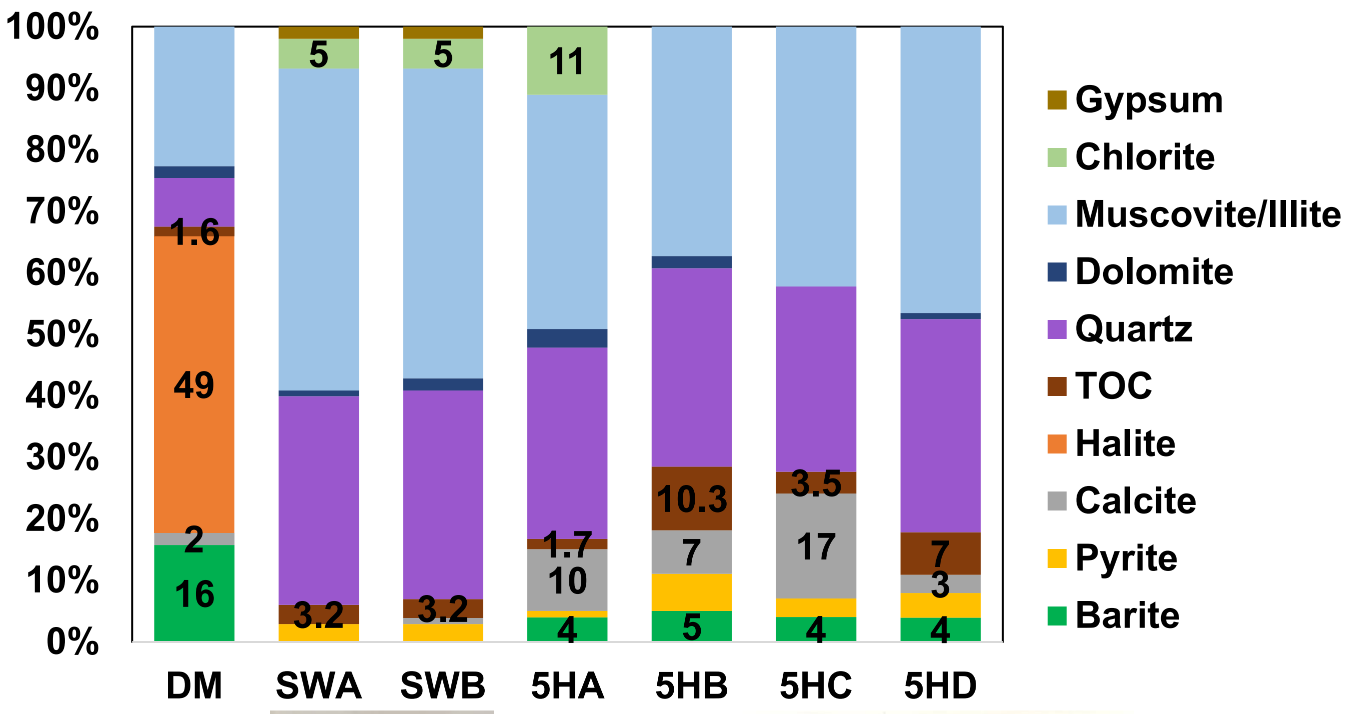
Drilling Mud

Known drilling fluid composition:
30-60% Barite
10-30% n-dodecane
10-30% alkenes
10-30% tetradecane
10-30% N-Undecane
Misc. fatty acids

Stuckman, M. Y., et al. (2019). Journal of Natural Gas Science and Engineering **68**: 102922.

MSEEL: Solid Characterization

Semi-Quant XRD



XRD & TOC analysis

- DM: High halite (NaCl) and barite ($BaSO_4$)
- SWA&B: no barite, low calcite
- 5HA: 7758 – High clay, low TOC, mod calcite
- 5HB: 9358 – high pyrite, high TOC
- 5HC: 10638 – high calcite
- 5HD: 10958 – low calcite, mod TOC

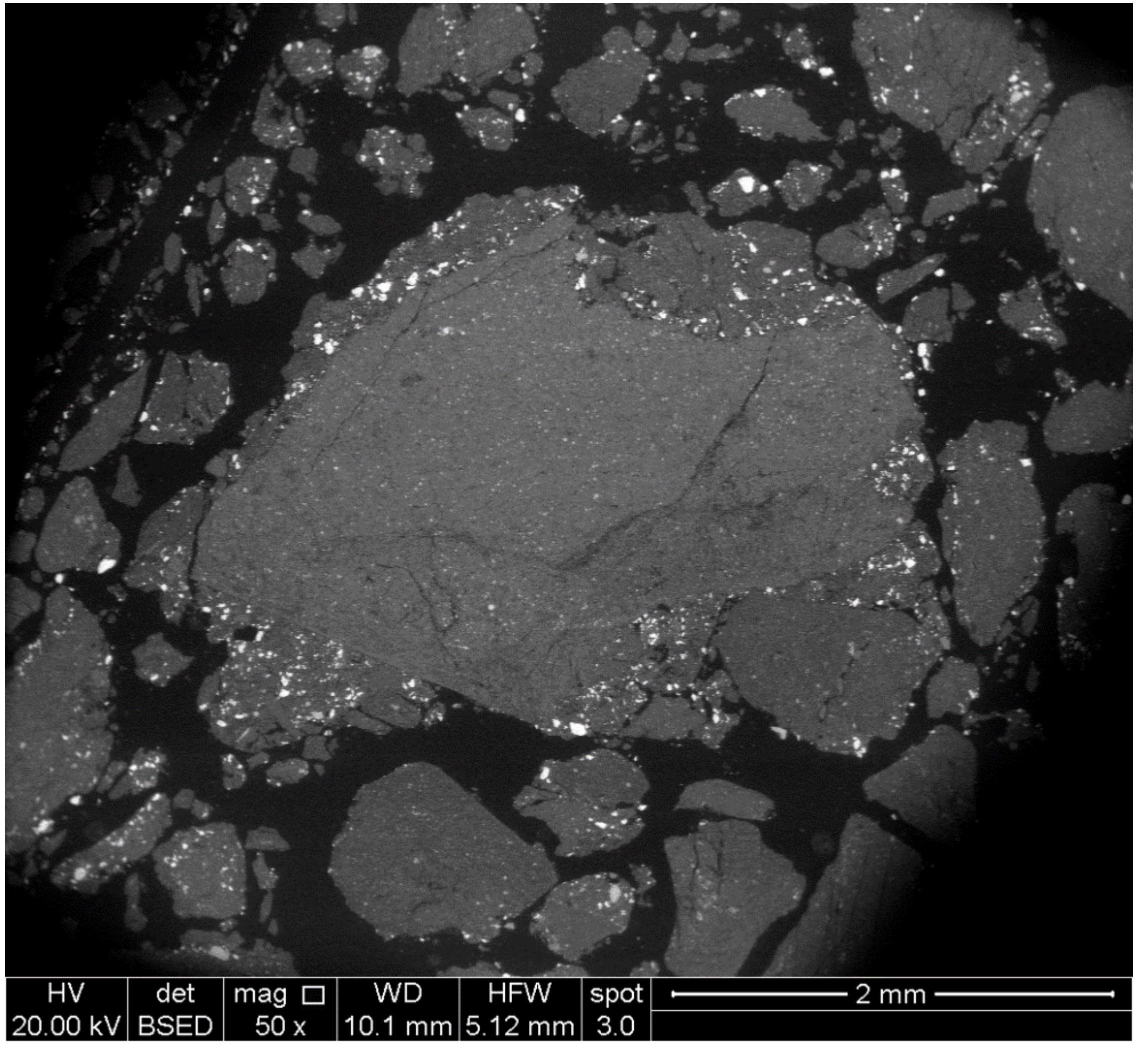
Elemental Analysis

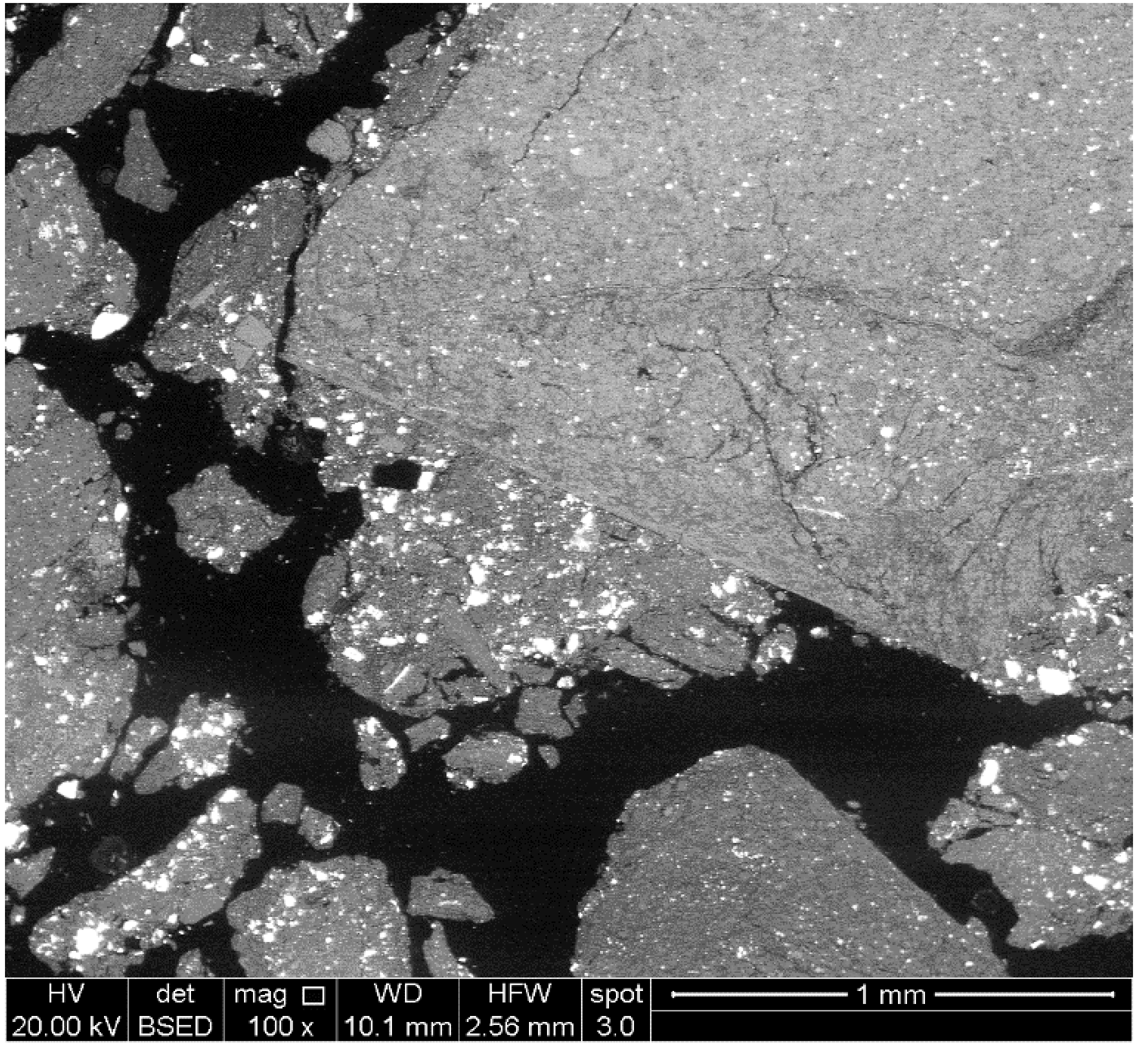
- Trace metal concentrations in core samples (SWA, SWB) are similar to those in drill cuttings, except Ca, Ba and Sr
- 5HB contain highest As, Cd, Co, Cu, Fe, Mo, Ni, Pb, Sb, U, B and Zn in our collected samples

Stuckman, M. Y., et al. (2019). Journal of Natural Gas Science and Engineering **68**: 102922.

Characterizing the Cuttings

Muds/fine coats the rock fragments



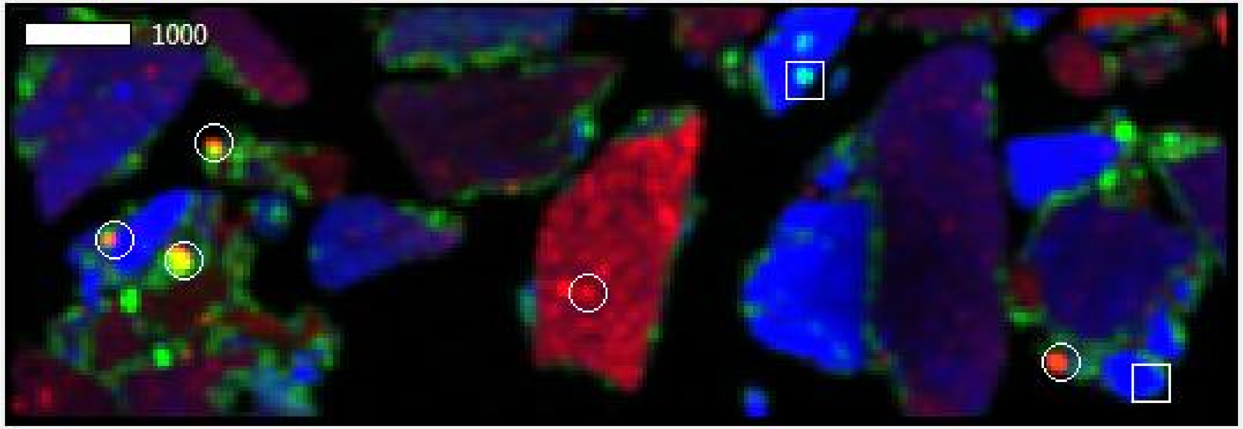


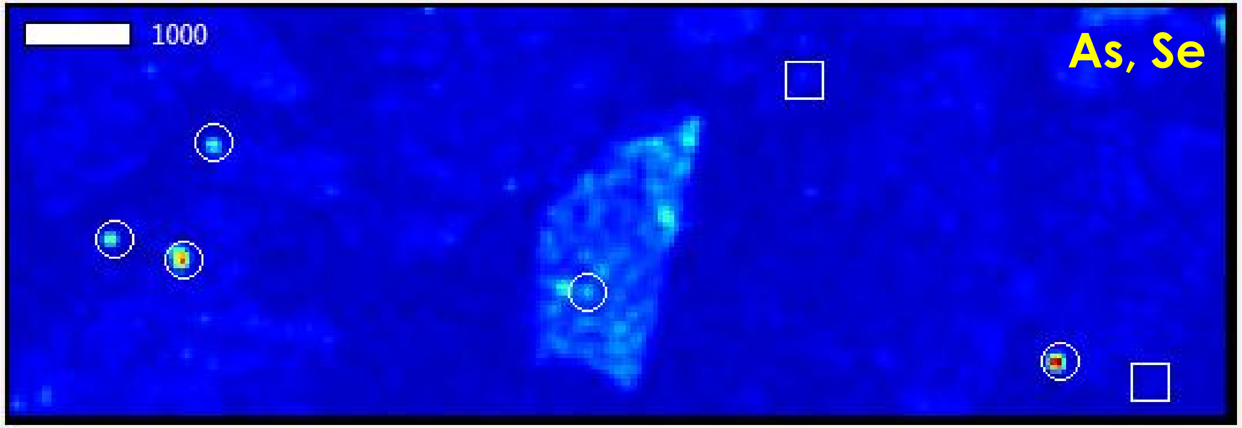
Elemental Maps for Drill Cuttings

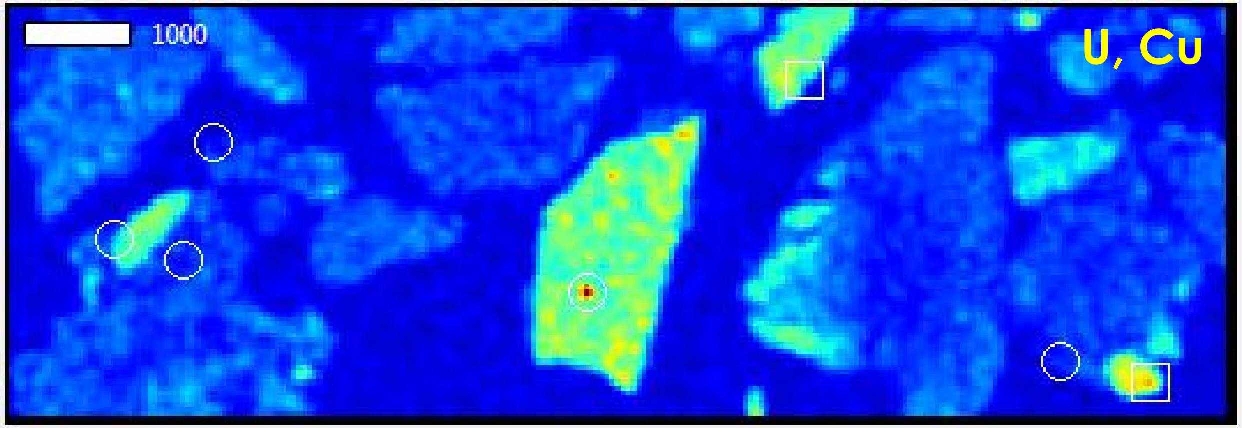
Drill cuttings contain shale cuttings and barite particles from drilling mud (DM) with 1-100 μm size

Trace metal deposition environments include pyrite and calcite

Fe in red, Ca in blue, Ba in green







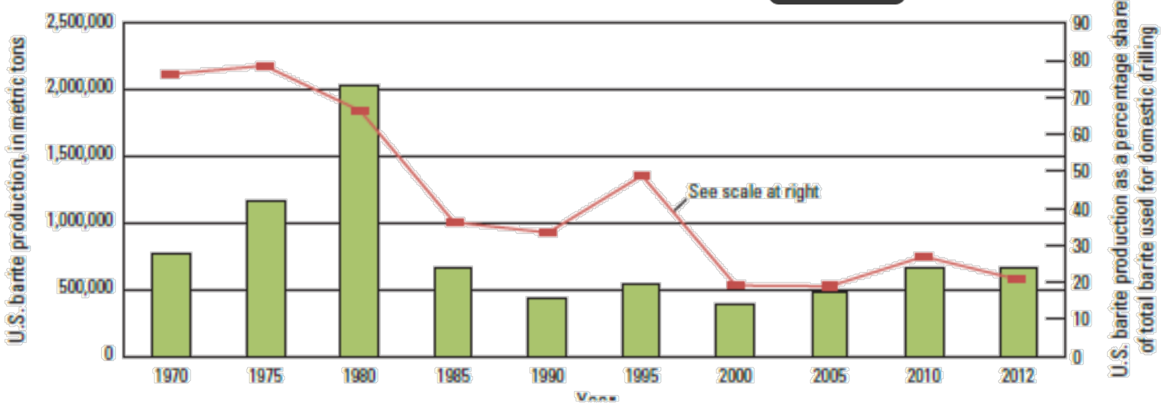
- o Trace metals with pyrite (e.g., As, Pb, Cu, U)
- ❑ Trace metals with calcite (e.g., U, Cu)

Coarse map data for 5HC collected at BL 10-2 at SSRL (50-micron beam size @ 18100 eV)

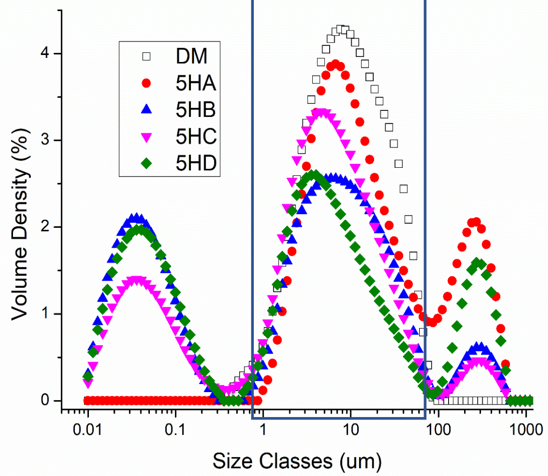
Barite

BaSO4

- Potential to recover barite from drill cuttings (1-100 µm) or improve recycling of drilling fluids on site
- Worldwide, 69–77% of barite is used as a weighting agent for drilling fluids in oil and gas exploration[1]
- The global production of barite is mainly from China (40%), India (17%), and Morocco (11%)[2]



US barite production and production as percentage of total barite used for drilling[1]

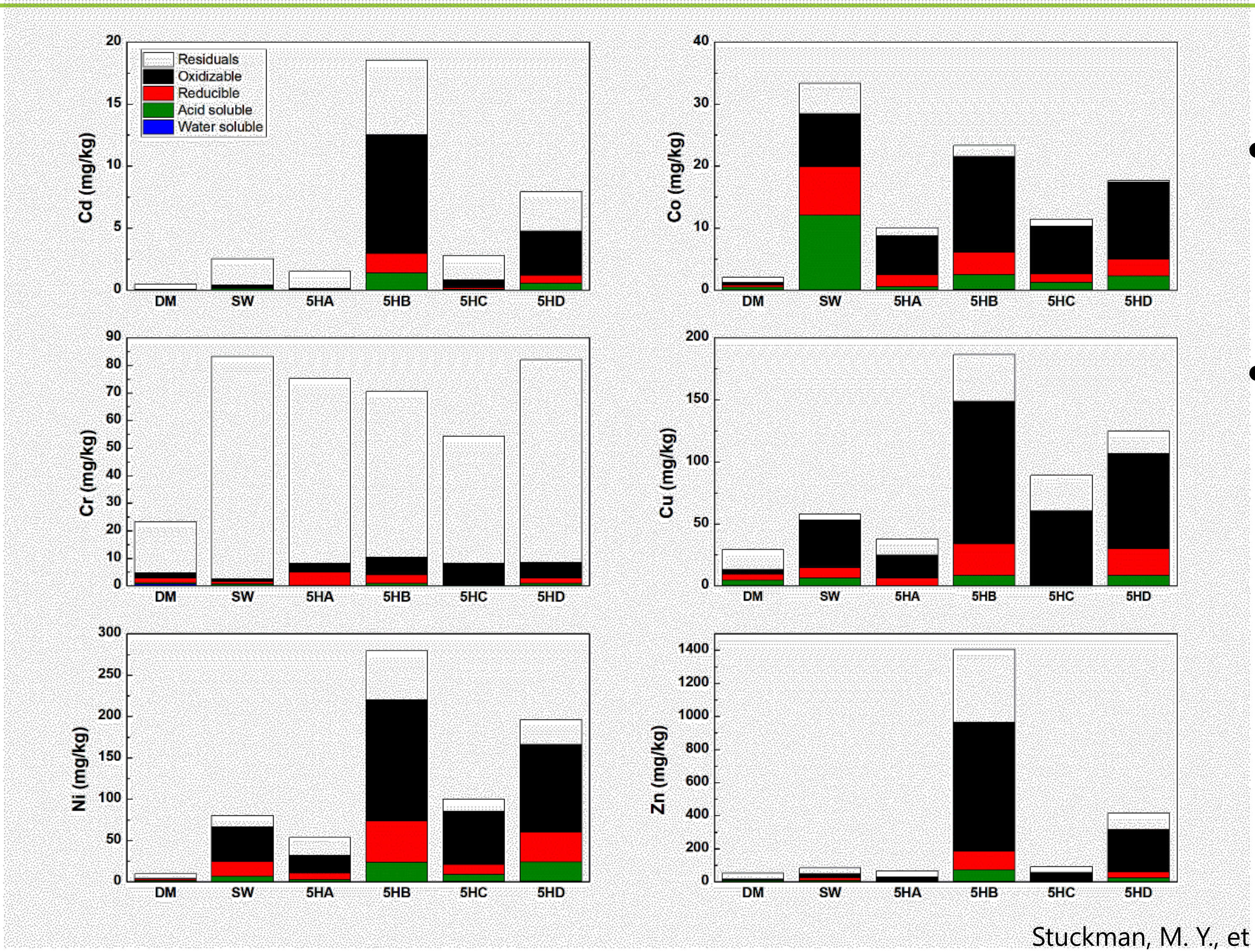


Barite powder for preparation of drilling mud[2]

1. Bleiwas, D.I., and Miller, M.M., 2015, Barite—A case study of import reliance on an essential material for oil and gas exploration and development drilling: U.S. Geological Survey Scientific Investigations Report 2014–5230, 6 p
2. https://en.wikipedia.org/wiki/Baryte

U.S. DEPARTMENT OF ENERGY

CM Results from Sequential Extraction



- CM enriched in 5HB with high pyrite and organic carbon.
- 70% Co, Ni, Zn, Cu extracted from "Oxidizable and organic" phases from drill cuttings

Stuckman, M. Y., et al. (2019). Journal of Natural Gas Science and Engineering **68**: 102922.

Environmental impacts of drill cutting disposal

NATIONAL ENERGY TECHNOLOGY LABORATORY

Leaching characteristics under different disposal scenarios

On-Site Burial & Road Fill — **Release by rain water**

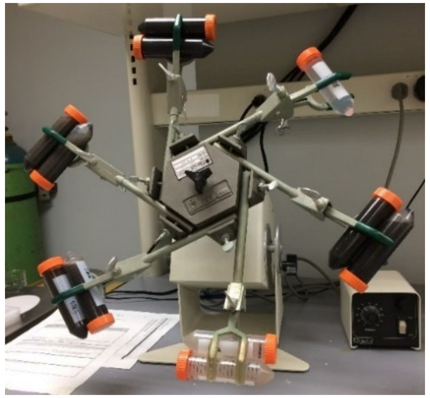
- USEPA 1311: Synthetic Precipitation Leaching Procedure (SPLP): Synthetic acid rain at pH 4.2, DI water adjusted by sulfuric/nitric acid

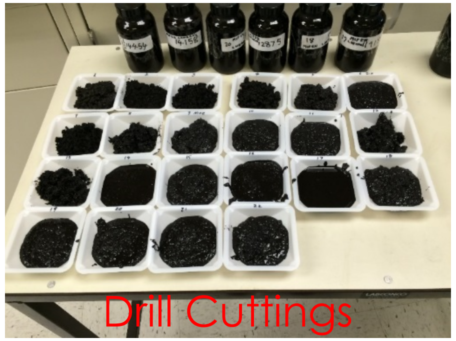
Landfill — **Release by landfill leachate**

- USEPA1312: Toxicity Characteristics Leaching Protocol (TCLP): Acetate-based synthetic leachate at pH 4.9
- USEPA 1320: Multiple Extractions

Framework Leaching — **Parallel Batch Extraction for broader disposal scenarios (pH, time, L:S)**

- USEPA 1313: As a function of extract pH
- Bioavailability Screening Test (Kosson, 2002): 50mM EDTA





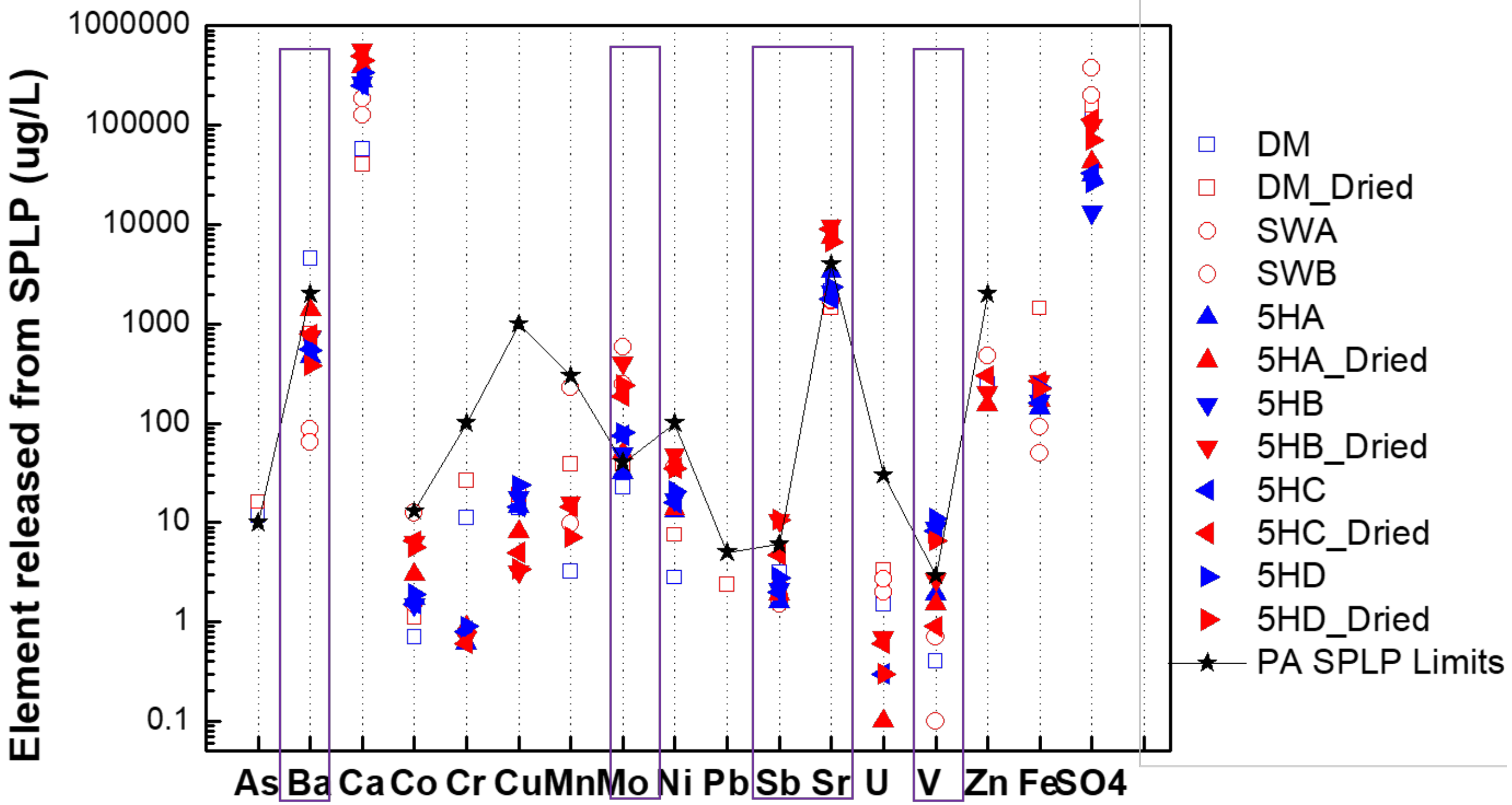
Stuckman M., et al. (2018), *proceeding of Unconventional Resources Technology and Exposition Conference,* Houston, TX, 23-25, July, 2018

MSEEL Regulatory Leaching; Wet vs. Dry Conditions

Regulatory Tests: TCLP: 0.11M Sodium acetate@ pH4.9, L:S=20:1; SPLP: DI water @ pH4.2

All passed TCLP (Toxicity Characteristics Leaching Protocol) tests simulating landfill conditions

Selected elements (e.g., Ba, V, Mo, Sr, Sb) from SPLP may be of concern mostly when the waste is dried



Stuckman M., et al. (2018), *proceeding of Unconventional Resources Technology and Exposition Conference,* Houston, TX, 23-25, July 2018

Drill Cutting Landfill Leachates Concerned Wastewater Treatment Plant

NATIONAL ENERGY TECHNOLOGY LABORATORY

https://stateimpact.npr.org/pennsylvania/2019/09/11/how-did-fracking-contaminants-end-up-in-the-monongahela-river-a-loophole-in-the-law-might-be-to-blame/

- Drill cuttings consist of about 40% of solid wastes in the *Belle Vernon Municipal Authority* landfill, which can contain naturally occurring radioactive materials, salts, and metals (e.g., Ba)
- "They were killing off our bugs. Our bugs are what treats the water," Kruppa from *Kruppa Sewage System*, said
- "We were discharging…into the Mon River higher than drinking water standards," Kruppa, said

How did fracking contaminants end up in the Monongahela River? A loophole in the law might be to blame

Reid Frazier

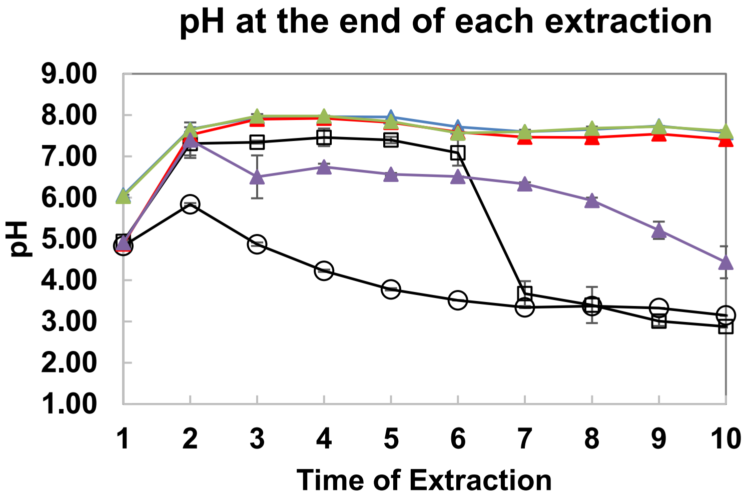
SEPTEMBER 11, 2019 | 5:00 AM

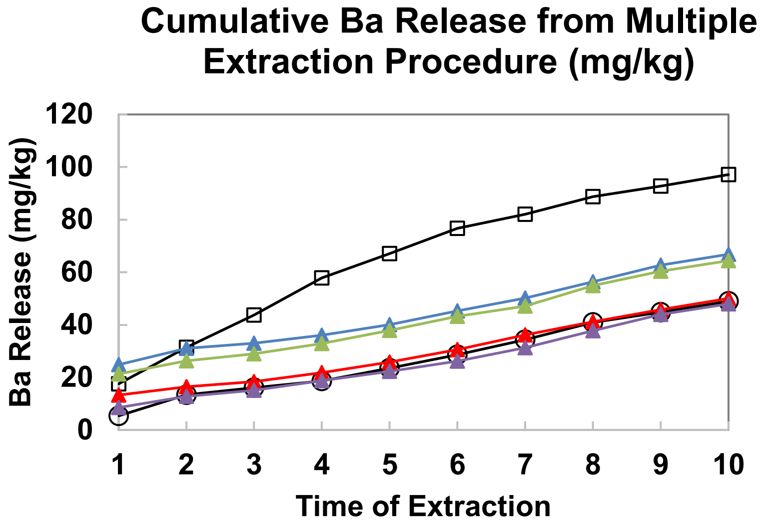
EPA1320: Multiple Extraction

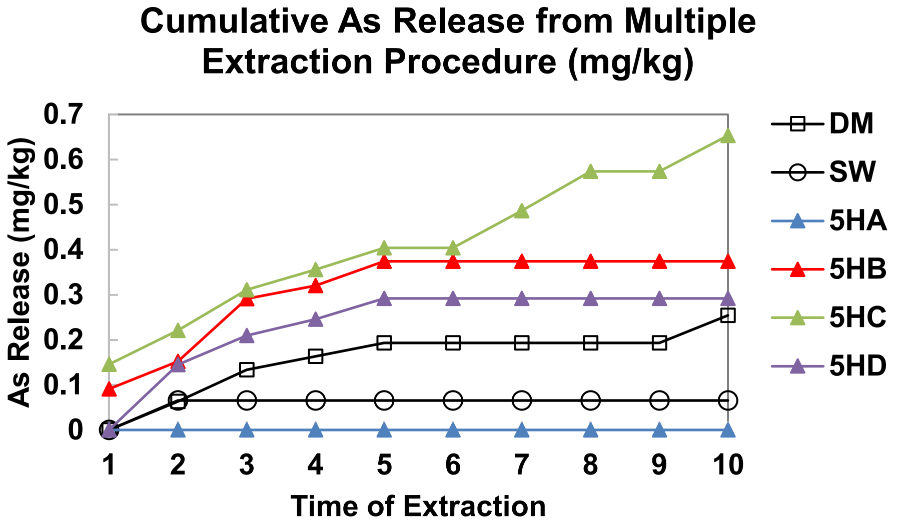
"Simulate leaching that a waste will undergo repetitive precipitation of acid rain on an improperly designed sanitary landfill" "Reveal the highest concentration that is likely to leach in a natural environment" (EPA1320)

Acetic Acid @ pH5 + 9 times synthetic rain @ pH 3

- Continuous long-term Ba release
- Cumulative release of oxyanions (e.g., As, Sb, V, and Mo), due to high pH buffer capacity (pH@ 7-8)
- 5HD had long-term release concern for Ni, Cd, Zn and Cr, due to low buffer capacity (3% Calcite)







Novel Waste Management: Soil Amendments

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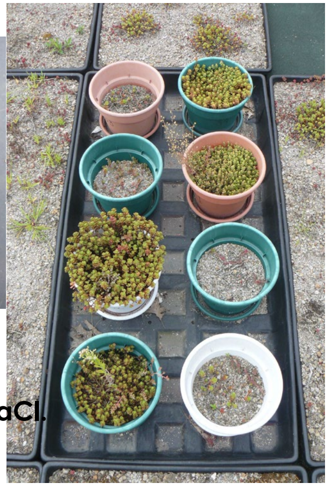
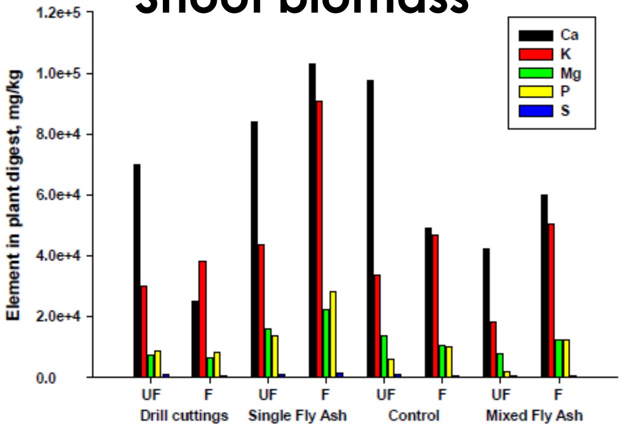
Use of waste as green roof substrate for plant growth

Lettuce seed germination was completely inhibited at 50% cuttings/soil (v/v), due to high NaCl

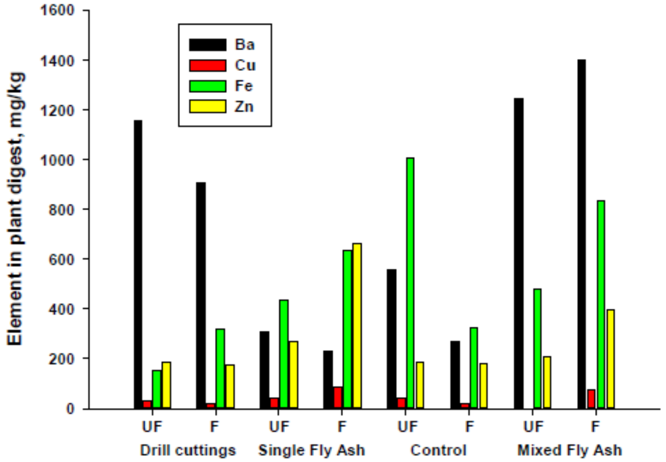


Shoot biomass



Preliminary Results

- **Preliminary evidence suggests that drill cutting serves a good growth substrate once NaCl is leached, but may result in high concentrations of <u>Ba in plant biomass</u>**
- **All drill cutting amended soils supported sedum growth over 16 months**



Edenborn, H. M., and Jinesh N. Jain. No. NETL-PUB-20276. National Energy Technology Lab.(NETL). In-house Research, 2016.

UF: unfertilized; F: fertilized

Conclusions

NATIONAL ENERGY TECHNOLOGY LABORATORY

Findings

- Trace metals in drill cuttings are co-localized with pyrite and calcite and become less mobile when pH is buffered by minerals in drill cuttings.
- Barite particles in drill cuttings are between 1-100 micron
- When drill cuttings are disposed of after drying, release of Ba, V, Mo, Sr and Sb become two - ten times greater compared to wet drill cuttings.
- Green roof plants were inhibited by high NaCl concentrations and accumulated Ba over time.

Management Suggestions

- Low content of pyrite and high content of calcite in drill cuttings are of low environmental concern; whereas high pyrite and organic content will host more **CMs** for potential recovery
- **Barite** might be separated and purified from drill cuttings
- Drill cuttings can be **kept wet** prior to disposal
- The optimal ratio of drill cuttings added to green roof plant substrates will depend on the initial salt concentration and relative metal mobility.

Acknowledgements

NATIONAL ENERGY TECHNOLOGY LABORATORY

It Takes a Village

Dr. Hank Edenborn – Green roof testing

Christine Thomas – Green roof testing

Samantha Berry – Summer intern extraordinaire

Dustin Crandall and Johnathan Moore – core logging and MSEEL background

Shikha Sharma – WVU and MSEEL liaison

Research supported by U.S. Dept. of Energy, Office of Fossil Energy

The synchrotron work was conducted on beamlines 2-3, and 10-2 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, through the Structural Molecular Biology Program, supported by DOE Office of Biological nmental Research and the National Institutes of

SSRL

Study 3: Brine Chemistry & CM in Fossil Fuel Wastewaters

NATIONAL ENERGY TECHNOLOGY LABORATORY

Measuring Targeted Chemicals in Messy Waters

Oil and Gas Brine

Acid Mine Drainage

Seawater Comparison
"Clean" Compared to the Oil, Gas, and Coal Related Waters

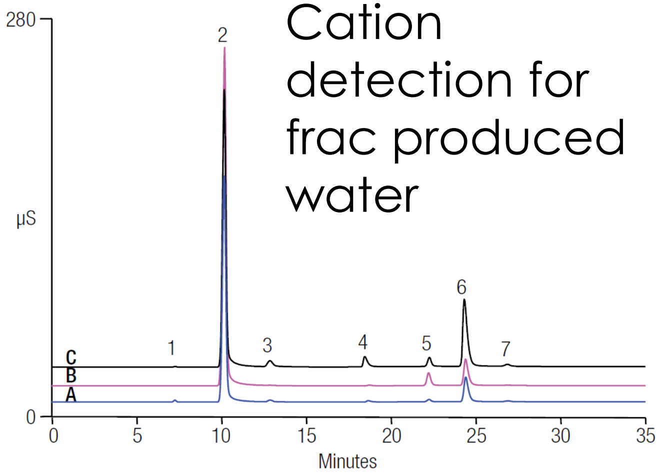
https://www.livingoceansfoundation.org/seawater-chemistry/

Ion Chromatograph (IC) Systems

Detection	Detector	Analytes
Cations	Conductivity	**Li+[1]**, Na+[2], NH4+[3], K+[4], Mg+[5], Ca+[6], Sr2+[7], Ba2+ [8]

Detection	Detector	Analytes
Anions	Conductivity	fluoride[2], chloride[13], nitrite[14], nitrate[17], bromide[16], bromate[12], phosphate[24], chromate[27], iodide[29], sulfate[21], thiosulfate[26], sulfite[20]
Organic Acids	Conductivity	acetate[4], lactate[3], formate[6], butyrate[3], propionate[4], pyruvate[8], succinate[15], oxalate[22], citrate[28]

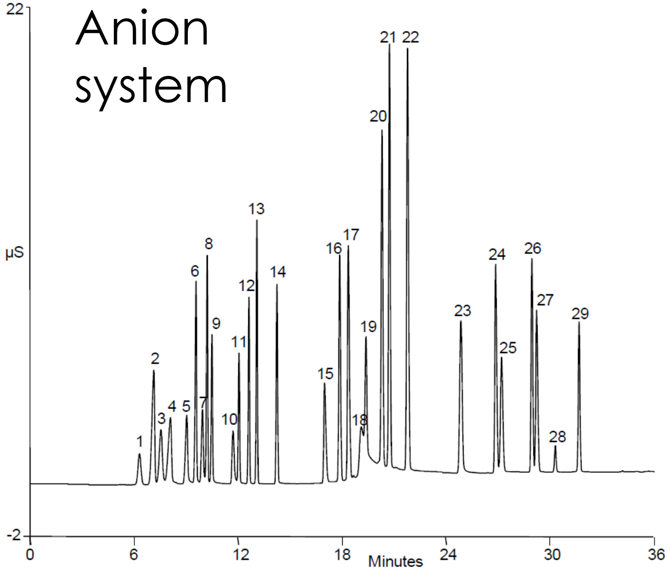
Intergrion



Cation detection for frac produced water

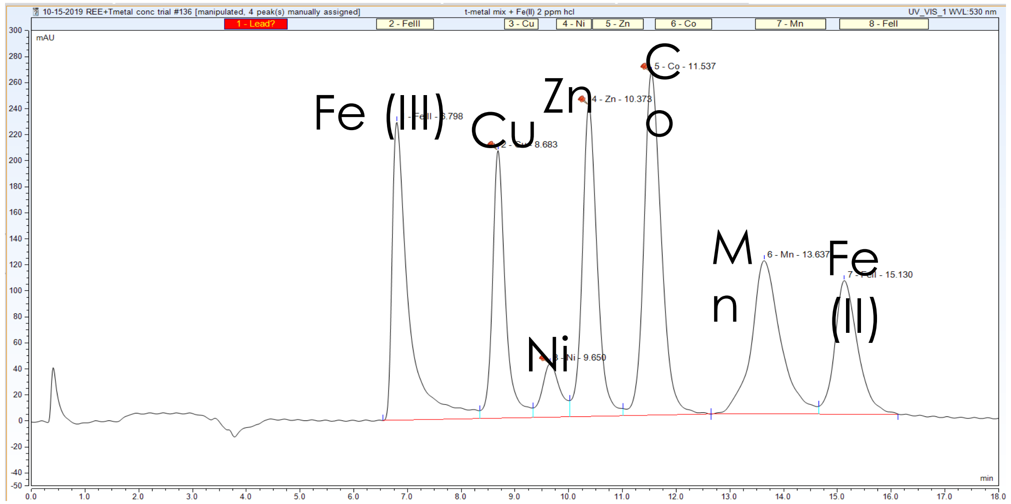
ICS-5000+

Anion system

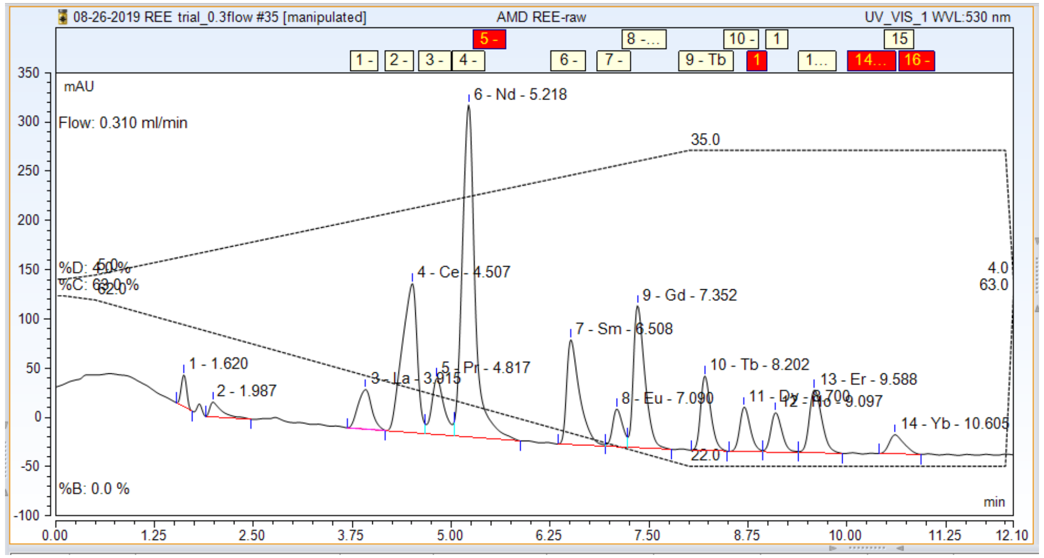


Newer Capacities on IC Systems

Detection	Detector	Analytes
Transition metals	UV-vis	[1]Fe^{3+}, [2]Cu^{2+}, [3]Ni^{2+}, [4]Zn^{2+}, [5]Co^{2+}, [6]Cd^{2+}, [7]Mn^{2+}, [8]Fe^{2+}
Rare earths	UV-vis	La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y
Sulfides	Electro-chemical	Sulfide and cyanide



Transition metals in brines[1]



REE in synthetic AMD[2]

UV-vis detector

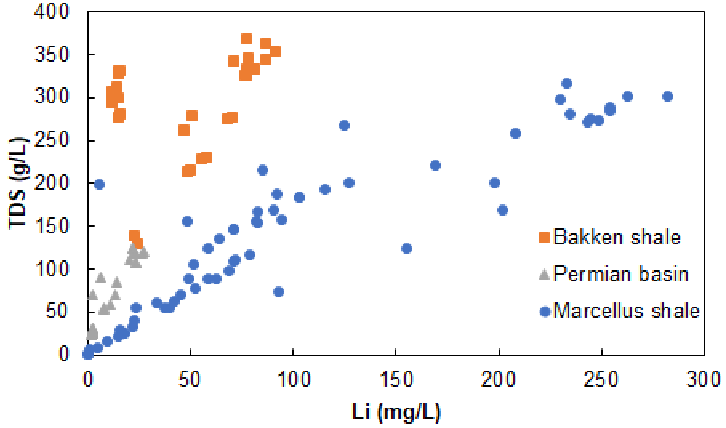
Electro-chemical detector (Ag-AgCl)

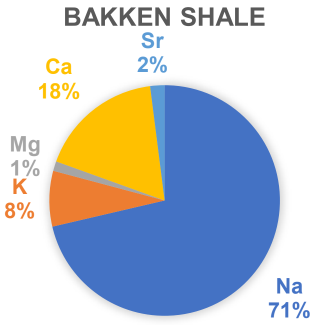
1: Miller, J., M. Stuckman, et al. (submitted), Simultaneous analysis of transition metal ions in fossil fuel associated wastewaters using chelation ion chromatography, *Journal of Chromatography*.

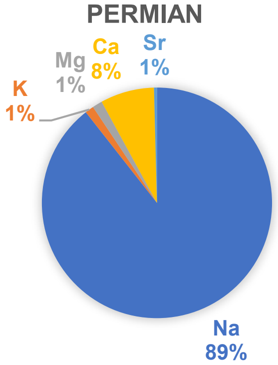
Five-Year Field Samples and New Findings

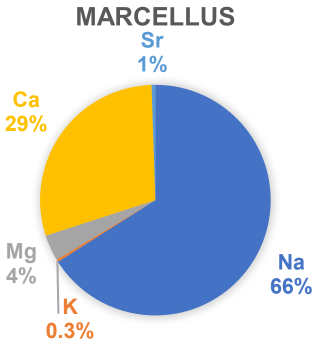
500 Samples: Bakken shale[1]: ~30/yr; Permian Basin EOR Oil field[2]: ~30/Yr; Marcellus Shale: ~200[3]

- Up to 300mg/L Li was found in Marcellus shale produced waters, comparable to the dominant source of Li mining, the brine ponds in Chile (1000mg/L)
- At the same TDS level, Marcellus Shale waters contain more Li compared to Bakken Shale and Permian Basin waters
- Marcellus shale brine contain high percentages of Ca and Mg, whereas Permian basin brine contain up to 89% Na.







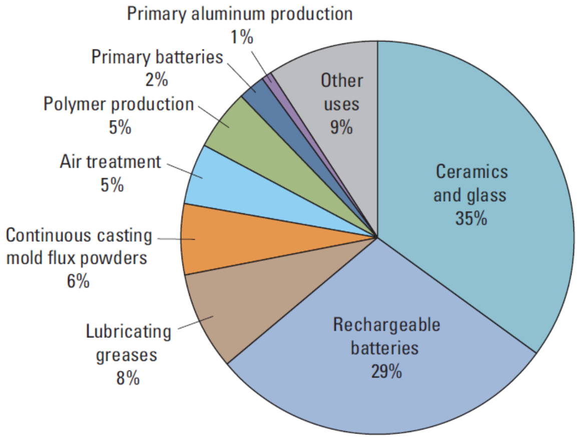


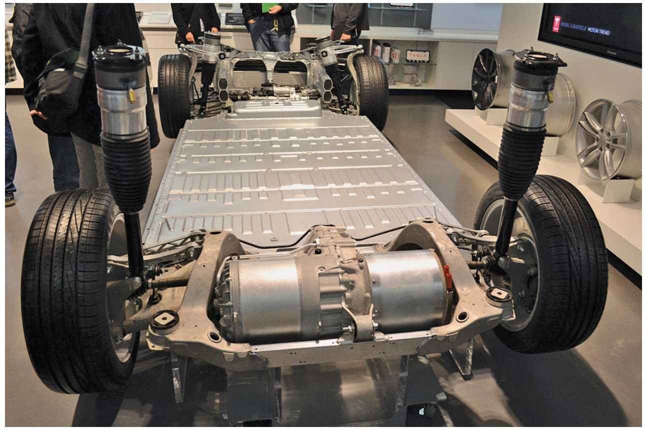
1: Tinker, K., J. et al., (2020). Frontiers in microbiology 11(1781).
2: Gardiner, J., et al. (2020). Applied Geochemistry 121: 104688.
3: Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179

Lithium Use and Extraction

Main Imports from Brine Ponds in Chile and Li-Pegmatite in Australia

Lithium-brine evaporating ponds at Clayton Valley, Nevada.
Li concentrates from 160ppm to 5,000ppm in 2 years[1]





Tesla electric car with 10-20 kg Li[2]

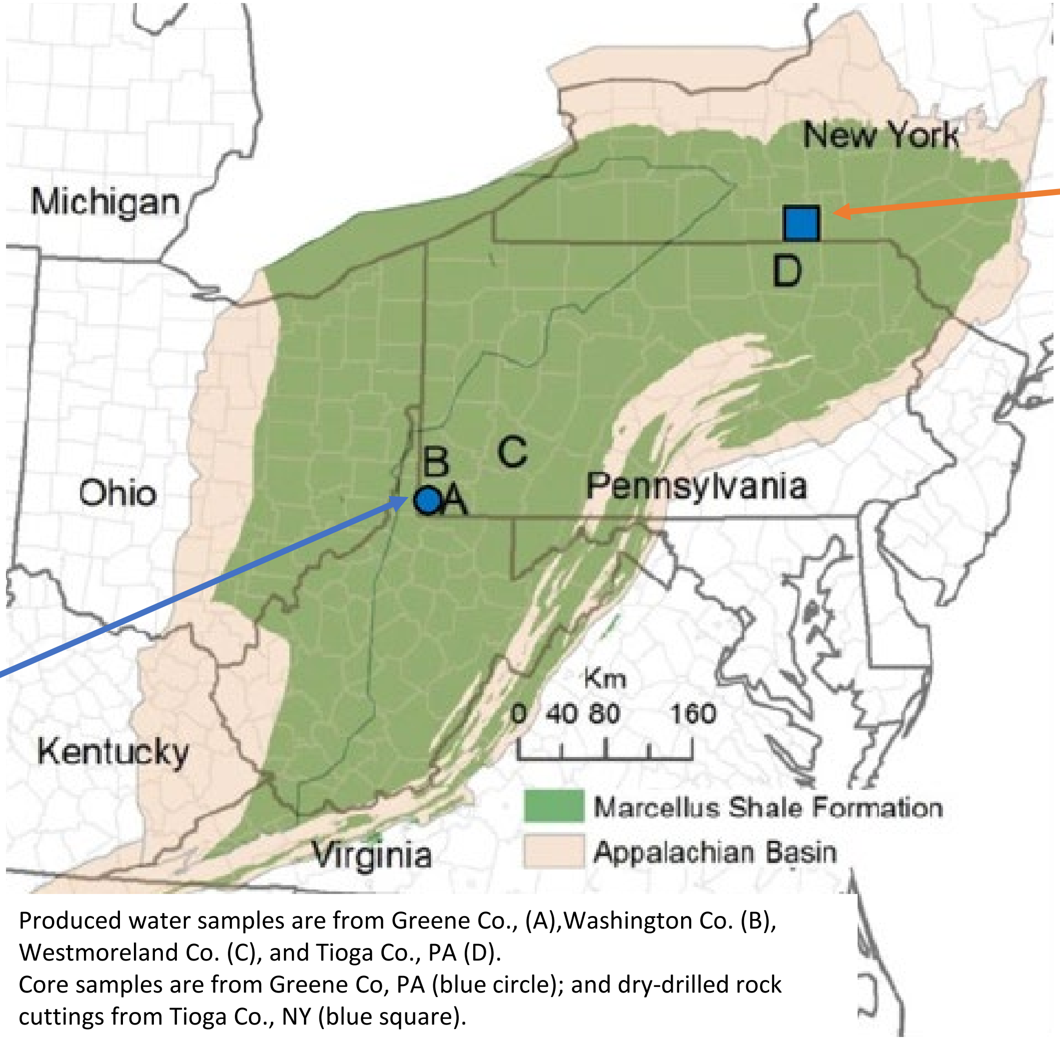
1. Bradley, D. C., et al. (2017). Lithium. Professional Paper. Reston, VA: 34.
2. http://commons.wikimedia.org/wiki/File:Chemetall_Foote_Lithium_Operation.jpg

Li Data in Marcellus Shale Produced Waters

Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179

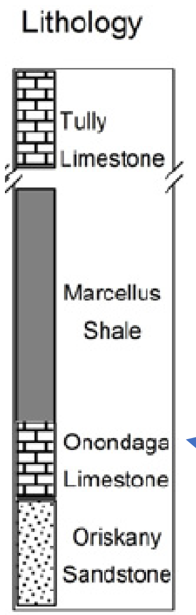
- *Clay minerals are the main sources of Li in organic-rich shale rock*
- *Li-rich formation water resulted from long-term alteration of volcanogenic ash*

- ***Southwestern PA:***
- ***Shale rock Li: 36-48 mg/kg***
- ***Li concentration: 18-233 mg/L***



Produced water samples are from Greene Co., (A),Washington Co. (B), Westmoreland Co. (C), and Tioga Co., PA (D).
Core samples are from Greene Co, PA (blue circle); and dry-drilled rock cuttings from Tioga Co., NY (blue square).

- ***North-central PA and NY***
- ***Shale rock Li:19-85 mg/kg***
- ***Li concentration: 169-282 mg/L***



Tioga ash layer and other ash layers

Other CM Work for Produced Waters

- A review paper on the Li recovery potential across different basins (produced water data needed)
- Other candidates: B and Sr in Permian basin: 1 – 100 mg/L range; Ba in Appalachian basin: 1-50 mg/L
- Li and CM recovery from produced water
  - "Streamlining The Process To Extract Lithium, Rare Earth Elements From Natural Brines" using carbon dioxide (CO2) as the only additive. Jinichiro Nakano, Anna Nakano, James P. Bennett https://netl.doe.gov/node/9370
  - Utilize existing oil and gas produced water treatment process for CM recovery (e.g., Li) and other beneficial use (e.g., construction materials), which is environmentally friendly and low-cost compared to traditional Li mining. (Proposal in review at NETL)
  - Fill up the knowledge gap as to whether Li recovery is economically viable for water treatment of produced waters from oil and gas industries

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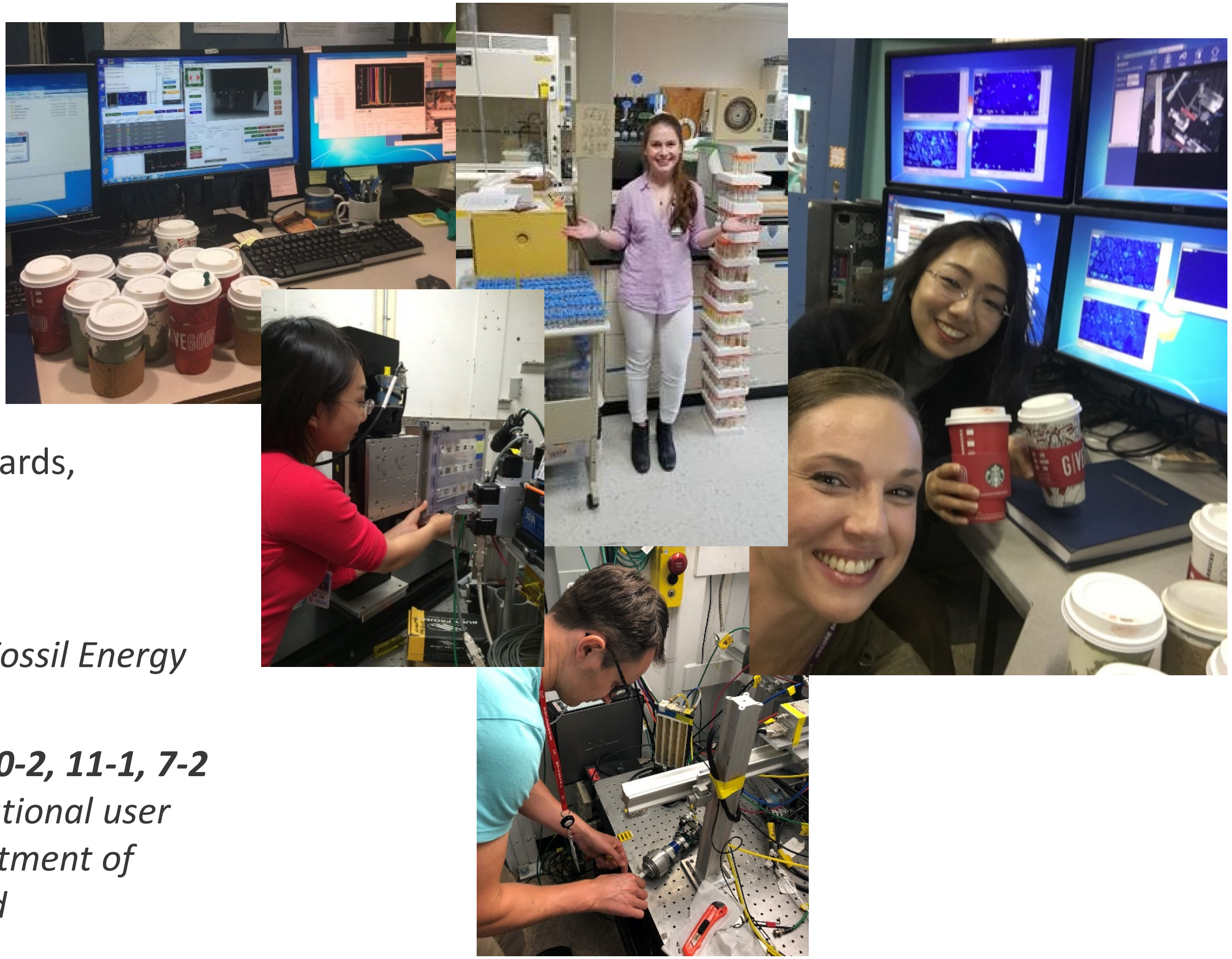

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