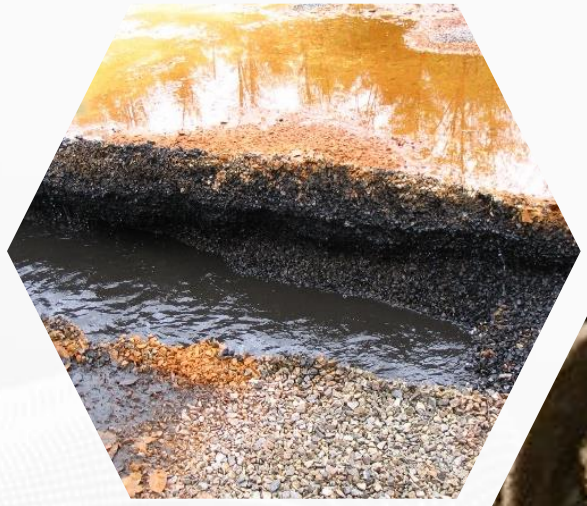
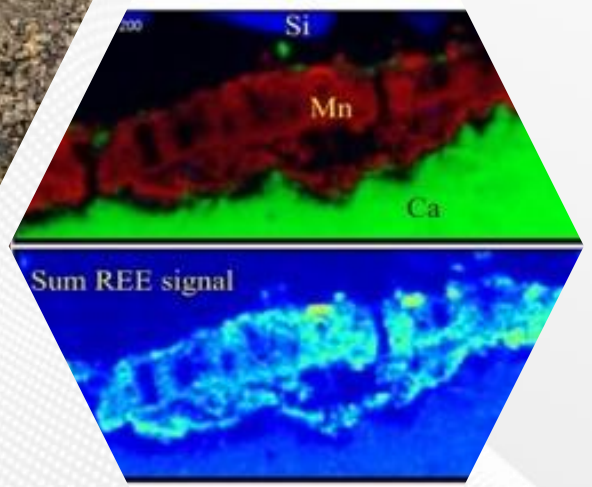
NATIONAL ENERGY TECHNOLOGY LABORATORY









Critical Mineral Recovery from Coal Mine Drainage: Impact of Mn/Fe/Al Chemistry

Mengling Stuckman[1*], Christina Lopano[1], Colleen Hoffman[1,2], Camille Shaffer[3], Ben Hedin[4], Charles Cravata III[5], Brian Stewart[6] and Rosemary Capo[6]

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ACS Fall 2026

U.S. DEPARTMENT of ENERGY

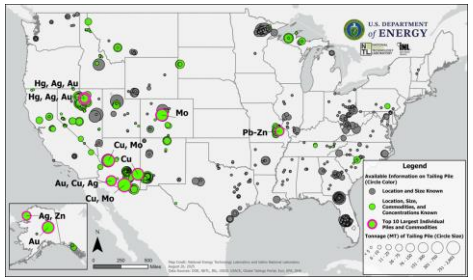
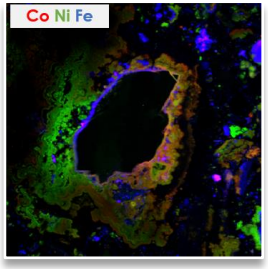
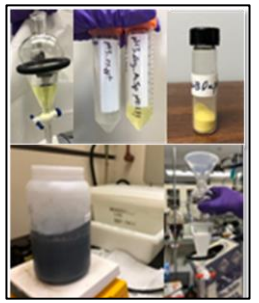
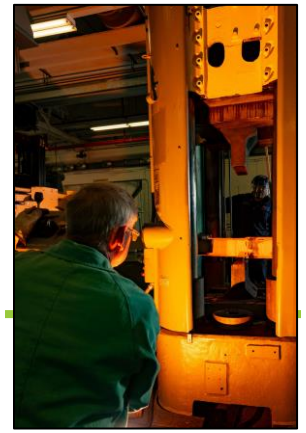
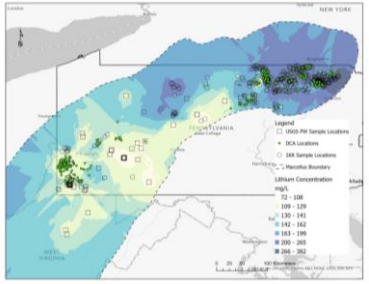
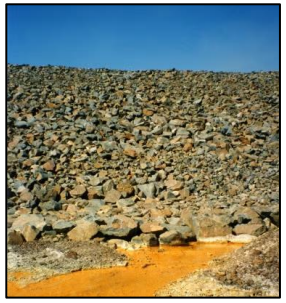
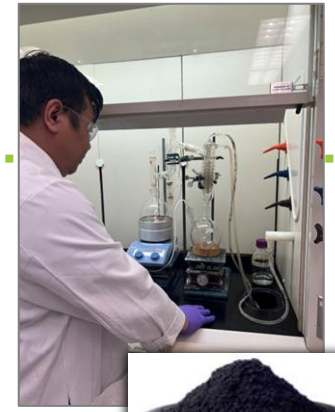
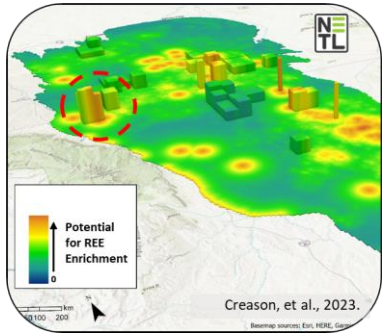
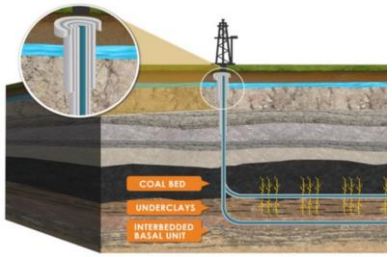
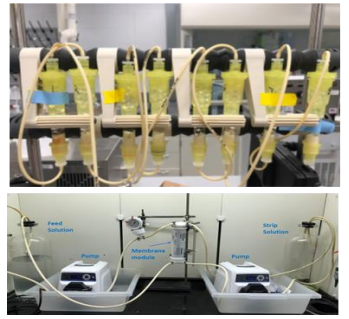
August 26, 2026

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NETL Center of Critical Minerals and Advanced Alloys

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	Upstream		Midstream		Downstream
	Identify *and* ***Prioritize*** *Feedstocks*	***Understand*** *Mineralogy, Speciation, Concentration*	***Produce*** *and Recover Minerals*	***Extract*** *and Separate Critical Minerals*	***Manufacture*** *High-Value Materials*
Solids					
Liquids					
In Situ					

National Critical Mineral and Material Prospectus v1

Creason, C.G., Conwell, C., Childress, T., Yesenchak, R., Cordero Rodriguez, N., Sullivan, B., Bauer, S., Hoover, K., Gupta, N., Jackson, Z., Mackey, J., Michels, A., Nakacwa, S., Miller, L., Olson, N., Sam, S., Boak, A., Perez, J., Suter, J., Guthrie, G., Montross, S., Mullen, J., Bromhal, G., and Wendt, A. (2025). Unconventional Feedstocks for Energy Critical Minerals and Materials: A National Prospectus – Energy Rare Earths and Lithium. Office of Fossil Energy, U.S. Department of Energy.



In situ Coal



Coal Refuse



Fly ash disposal lagoon



Acid Mine Drainage Produced waters



Fossil Energy feedstocks contain million of tons of REE oxides (REO)

Coal mine drainage: 10trillion L/yr flow, 20-500 tons REO/year, 20%-100% REO Based on 2020 U.S. demand

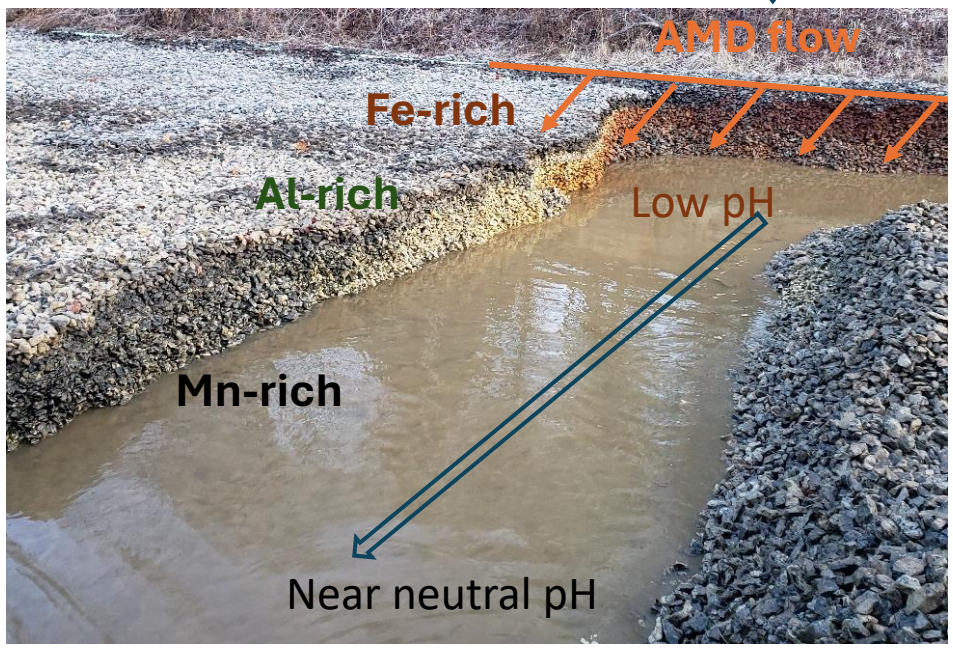
Feedstock Type	Bulk Feedstock Tonnage	Pr_2O_3 (t)		Nd_2O_3 (t)		Tb_2O_3 (t)		Dy_2O_3 (t)	
		low	*high*	*low*	*high*	*low*	*high*	*low*	*high*
In situ coal	7,000 Gt	10,000,000	20,000,000	50,000,000	100,000,000	1,000,000	3,000,000	10,000,000	20,000,000
Coal refuse	20 Gt	200,000	200,000	600,000	800,000	20,000	20,000	80,000	100,000
Coal ash	3 Gt	50,000	60,000	200,000	200,000	6,000	7,000	30,000	40,000
Coal mine drainage	10 trillion L/yr	30	100	100	500	20	40	30	200

Note: "Low" estimates are based on the first quartile value (25th percentile) of compiled REO concentration measurements, whereas "high" estimates are based on median (50th percentile) concentration values.

Table 1. Estimated unconventional feedstock tonnages and tonnages of REO ("low" and "high" estimates). Units of REO are in metric tons (t). See text for details on qualifying assumptions and caveats that should be considered when interpreting these data.

CM in Acid Mine Drainage (AMD) Treatment Systems





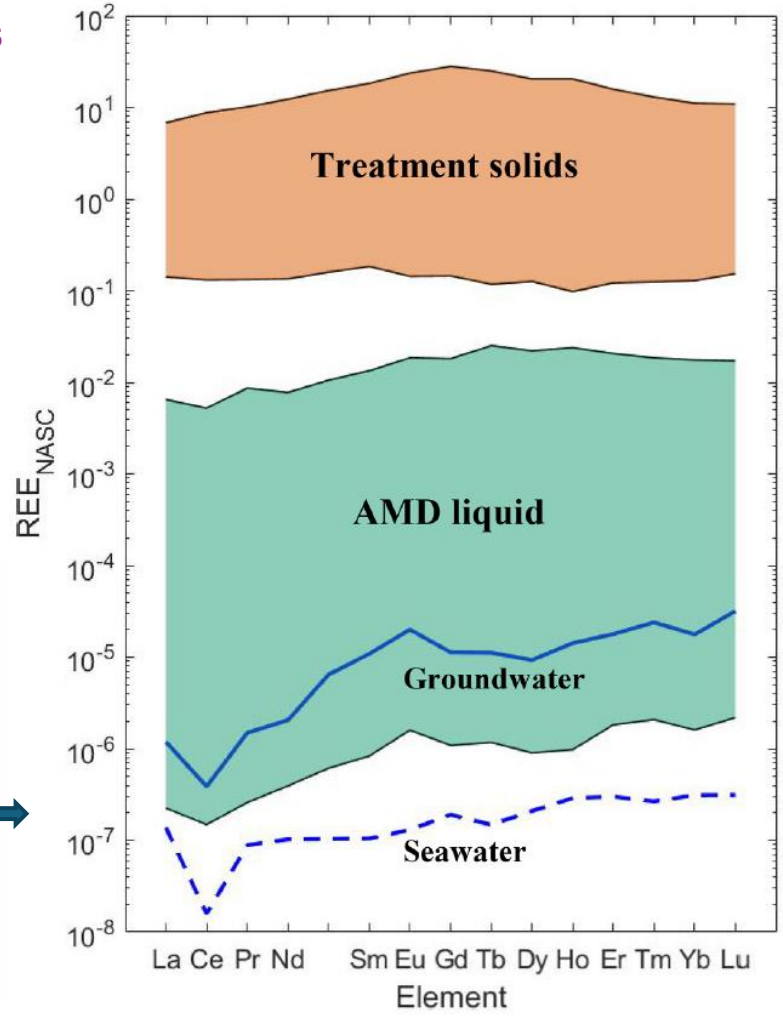
Passive Remediation Treatment: No chemical added, >200 systems in PA

Raises pH of water (Limestone beds)
Precipitate dissolved metals

- 90% REE sequestration rare earth element (REEs) precipitate with Fe, Mn, Al

~18,000 tons/year treatment solids produced: AMD solids

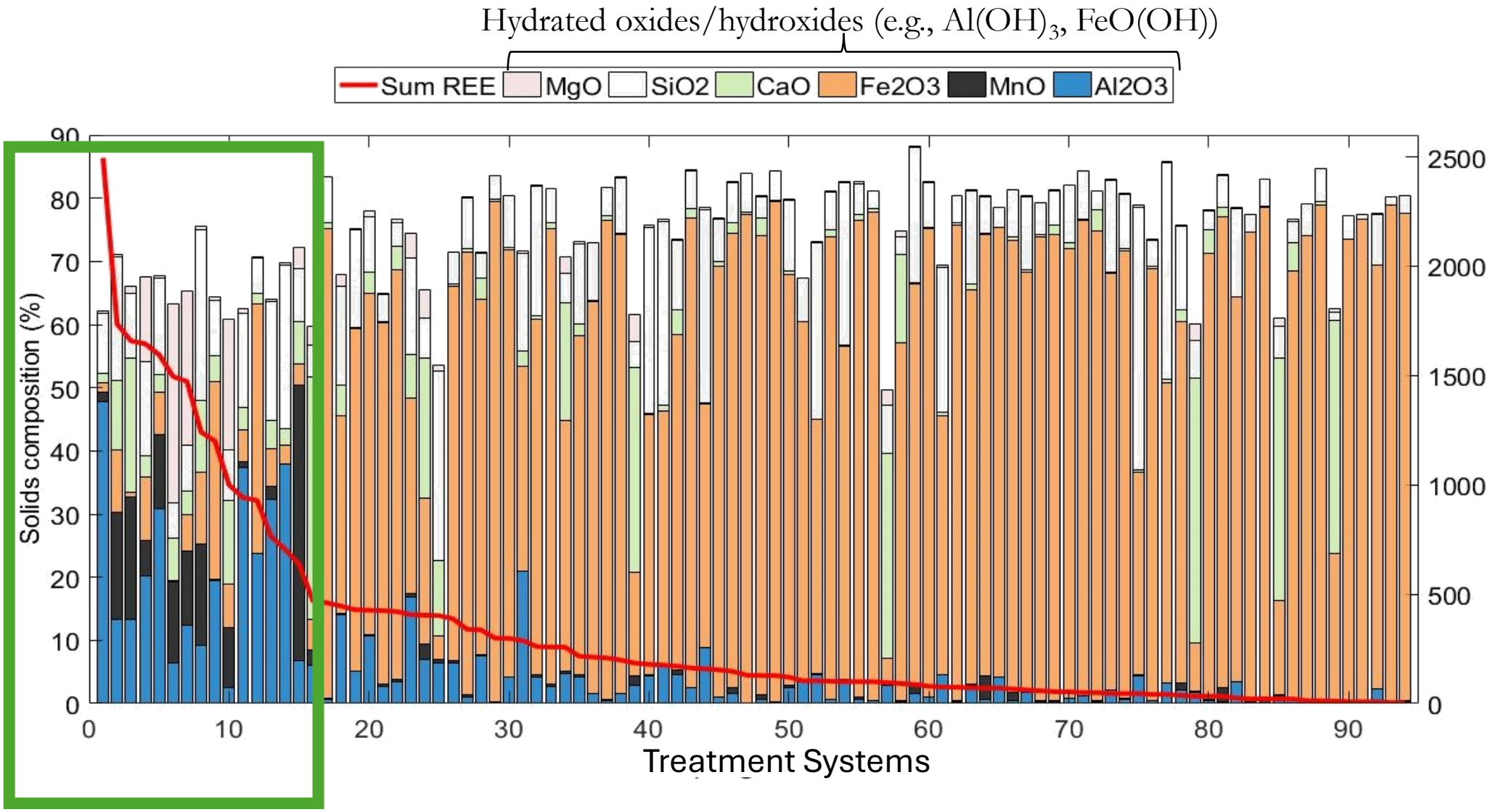




Hedin et al. (2019 & 2020), IJCG

https://www.thecentersquare.com/pennsylvania/article_f0a98eac-45ee-11ef-928c-332fe6bb1968.html

Compilation of ~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

Diverse chemical composition of 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
Mn 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

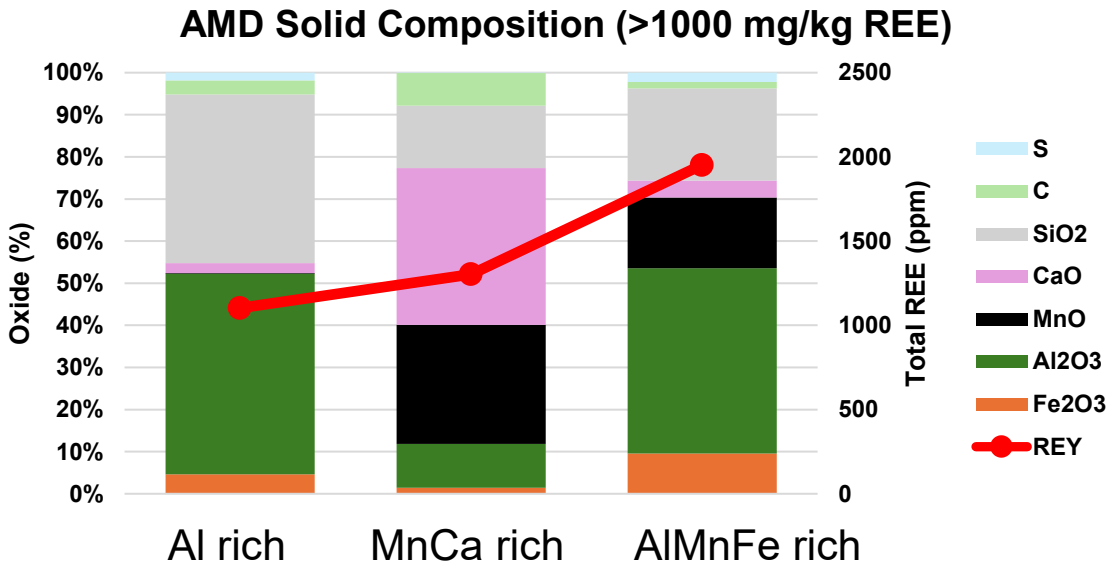


MnCa-rich solid





Al-, Mn-, Fe-rich solid



Hedin et al., IJCG, 2019; 2020

Bridging Upstream and Midstream

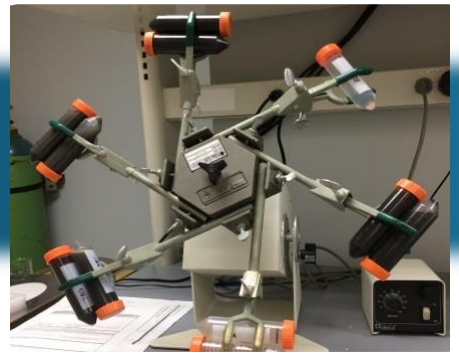
Characterization Drives Feedstock Prioritization and Informs Extraction Method Development

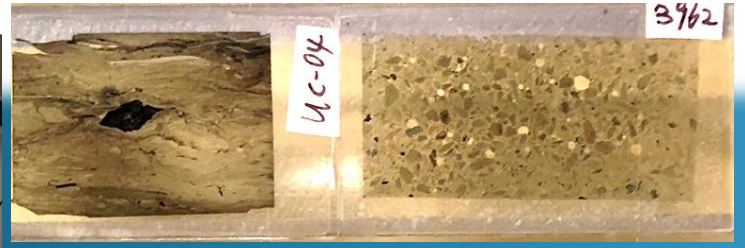


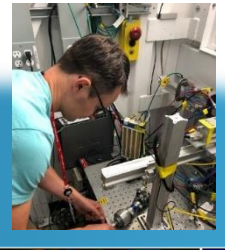
AMD solids



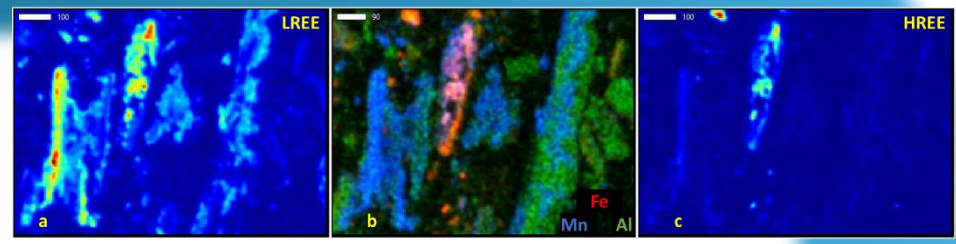
Fly ash





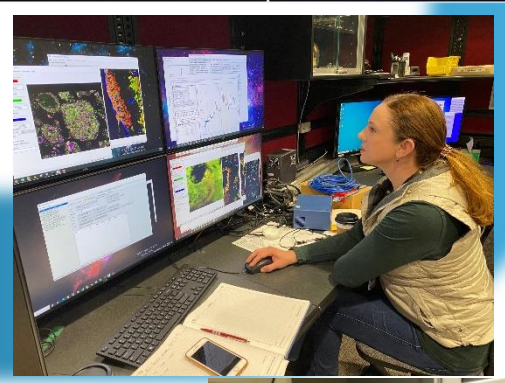




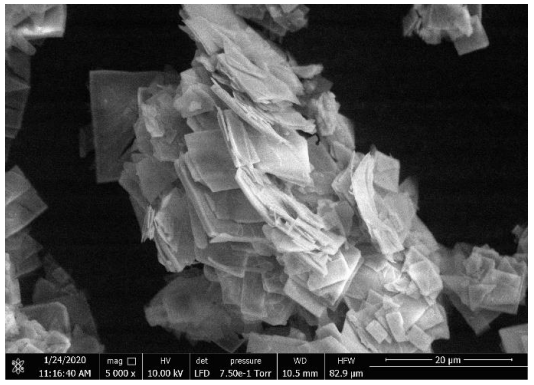


Utilize **characterization** of major CM-hosting solid fractions in different CCBs to **innovate targeted extractions** for efficient and economical REE recovery.

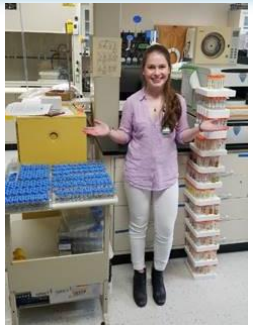
This study: REE (Ce) and Co in Al/Mn/Fe oxides

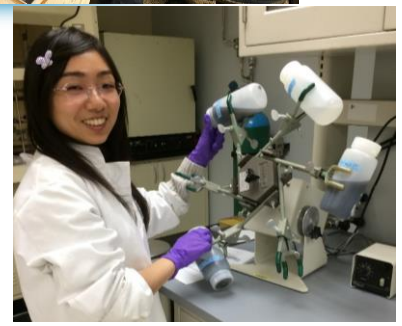


96wt% Pure Rare Earth Oxide (REO)



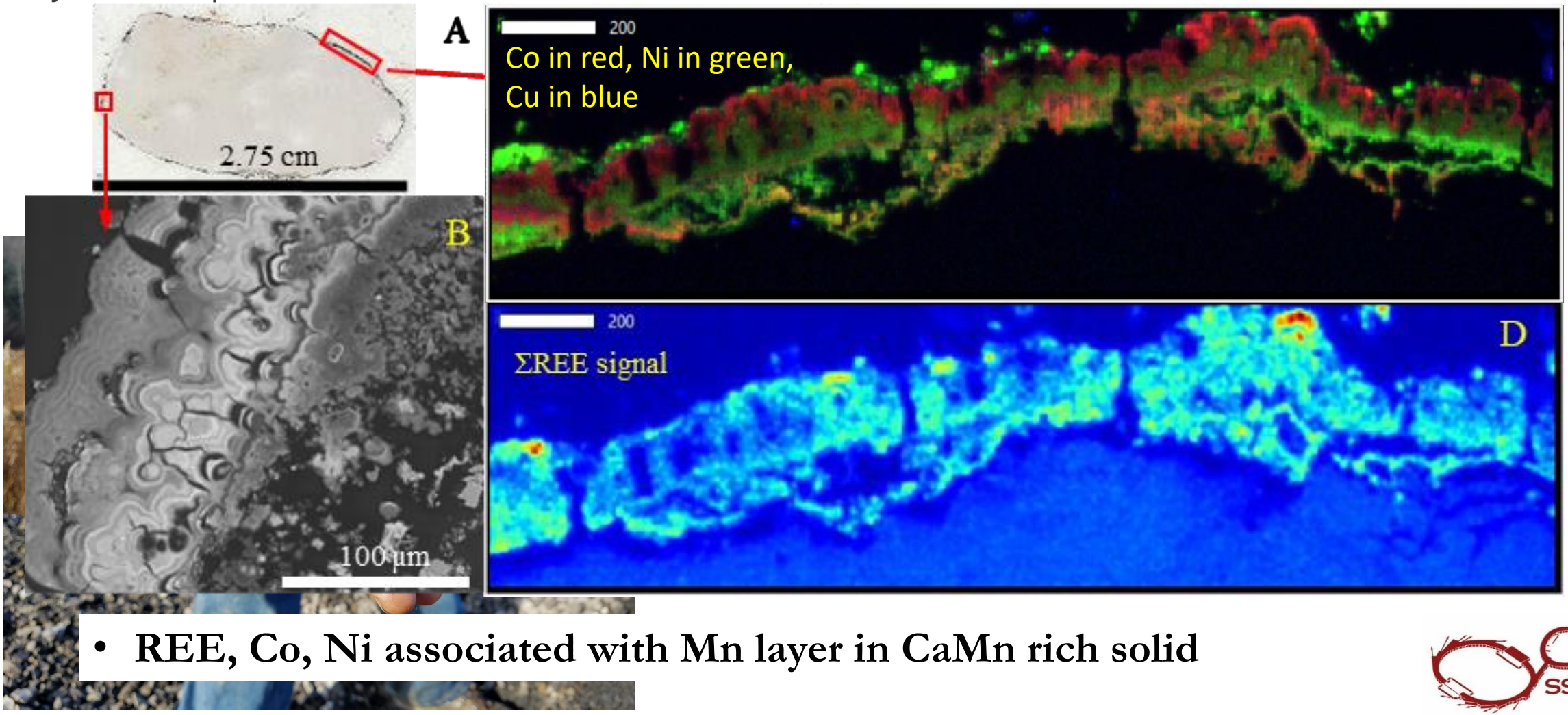






CM distribution in Mn-rich Solid

- Synchrotron μXRF



- **REE, Co, Ni associated with Mn layer in CaMn rich solid**

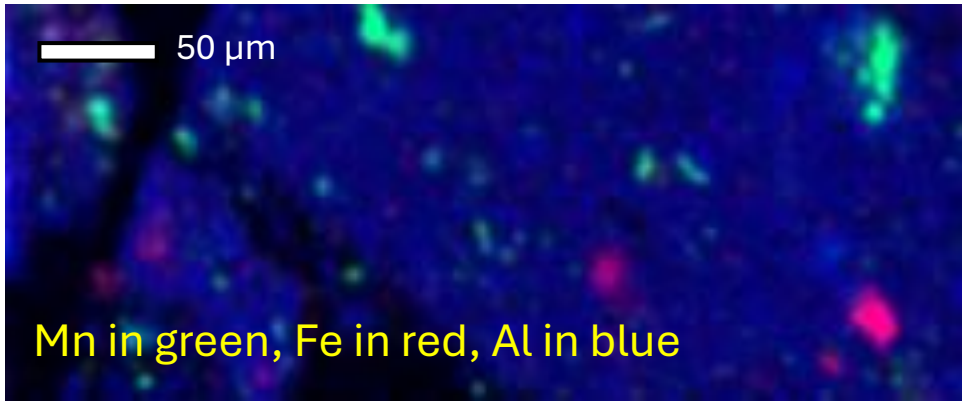
Hedin et al., IJCG, 2019

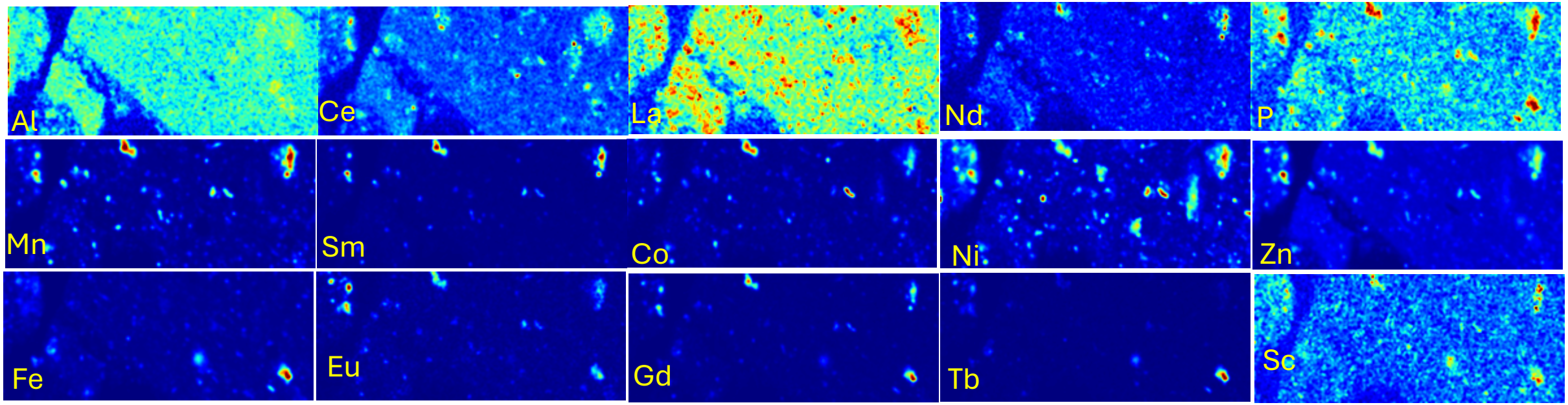
CM distribution in Al Rich Solid

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









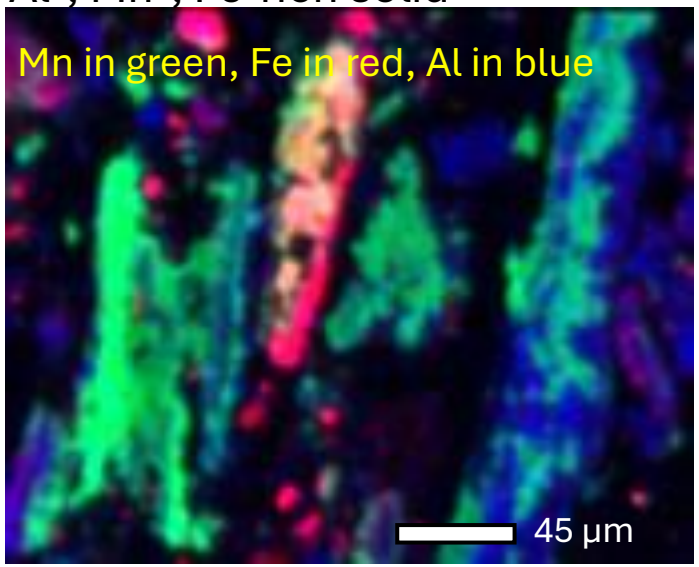
Hedin et al., Chemosphere, 2024

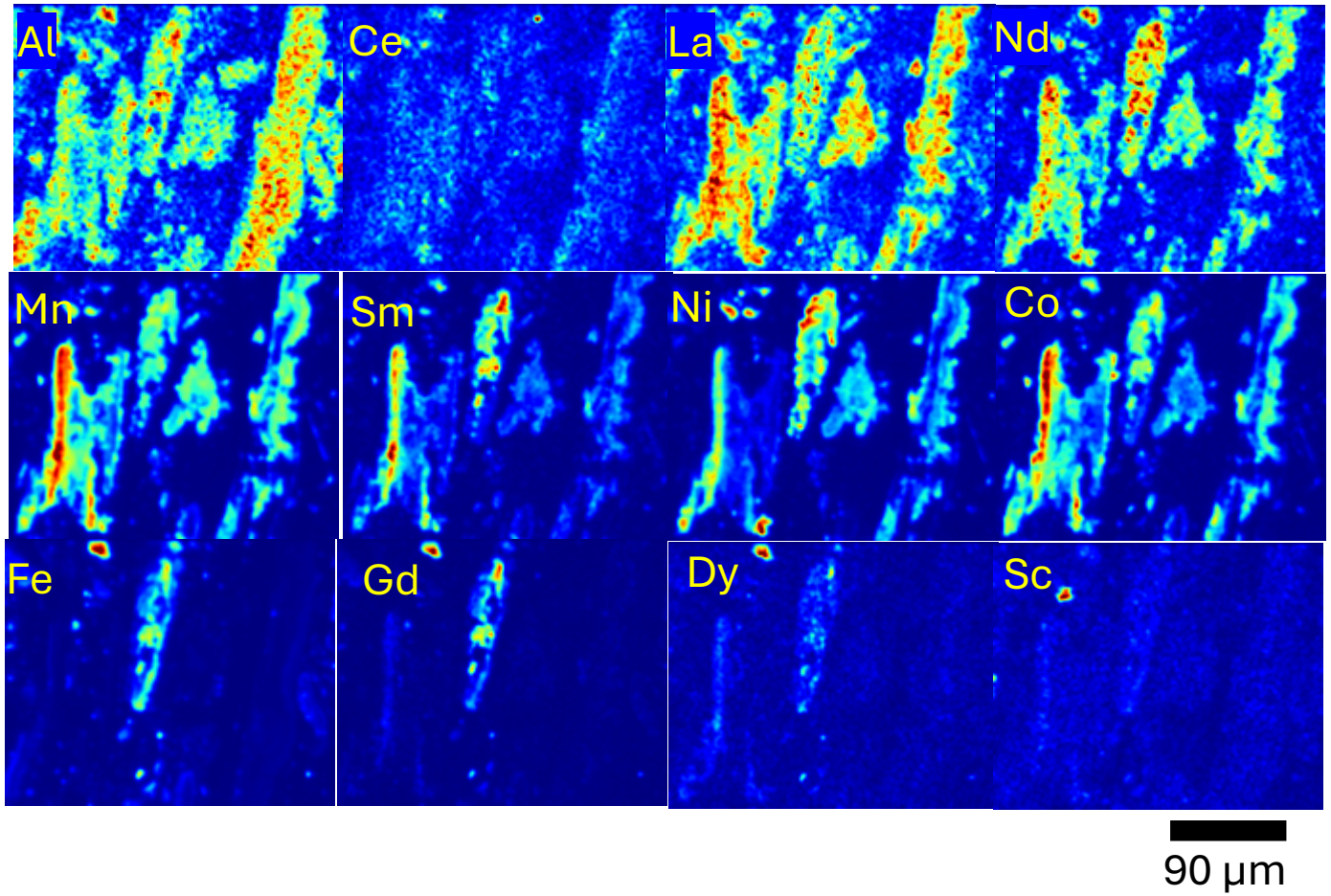
CM distribution in AlMnFe-rich solids

- 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



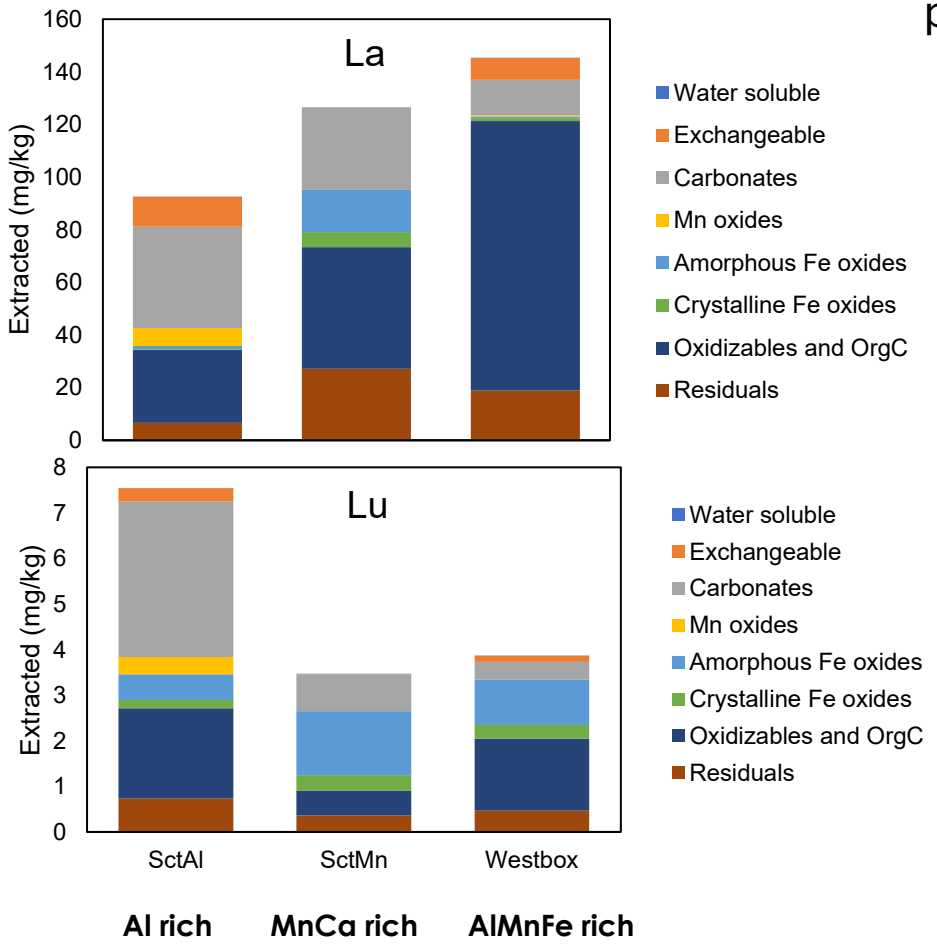


Hedin et al., Chemosphere, 2024

REE in Sequential Extraction and Geochemical Modeling

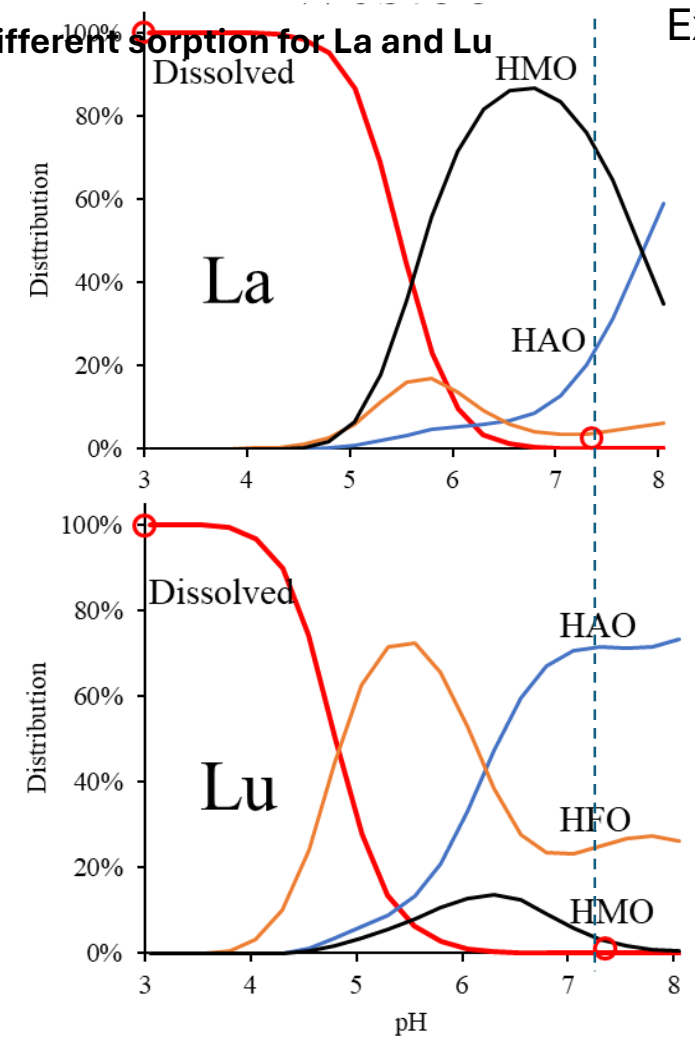
More than 80% REY (Al/Mn) extracted

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



PHREEQ-N-AMDTreat+REYs developed by C. Cravotta (2022)

Different sorption for La and Lu



Example of AlMnFe-rich solid

100% precipitated at effluent pH (7.2)
Adsorbed mainly on manganese hydroxides(HMO) and alumina hydroxides (HAO)

100% precipitated at 0effluent pH (7.2)
Adsorbed mainly on Mn hydroxides (HMO), Al hydroxides (HAO) and ferric hydroxides (HFO)

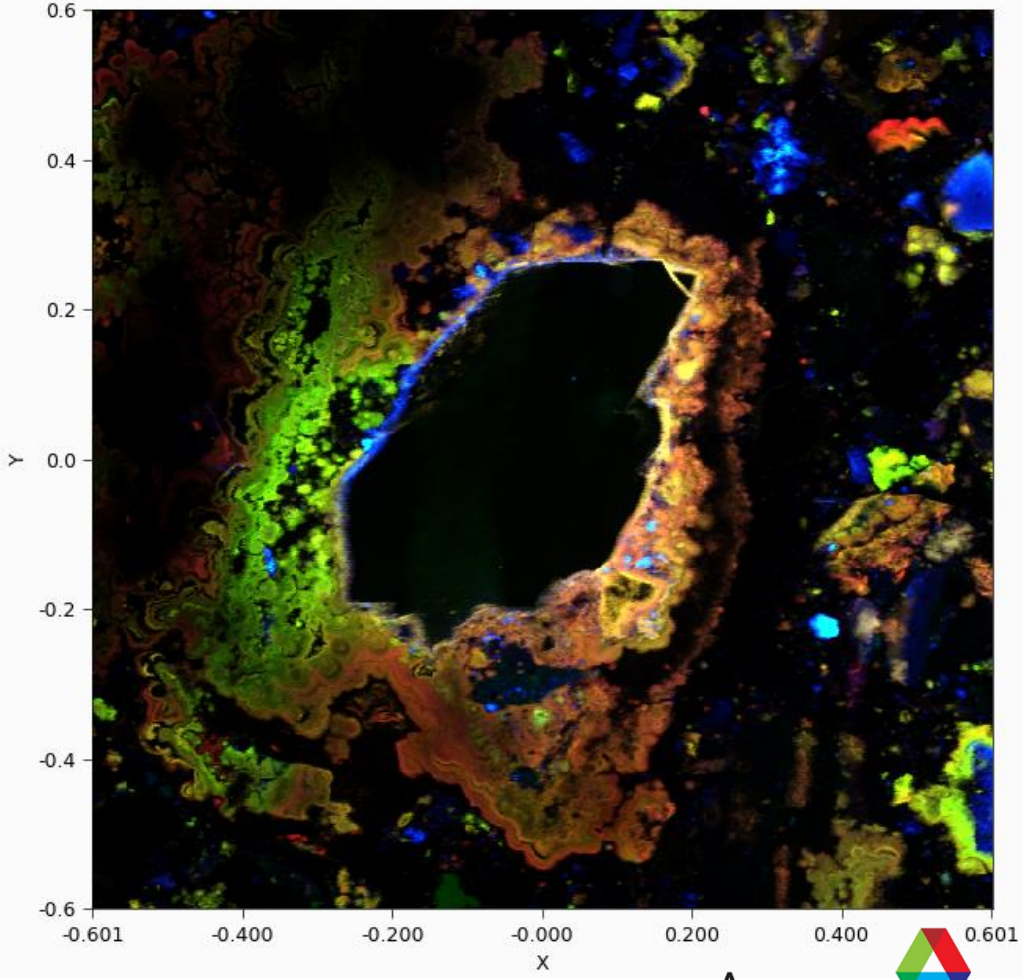
https://www.usgs.gov/software/interactive-phreeq-n-amdtreatreys-water-quality-modeling-tools-evaluate-potential

Hedin et al., Chemosphere, 2024: Tasker 2026; Boothe-Lordon et al. (2026)

CM distribution Summary

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

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



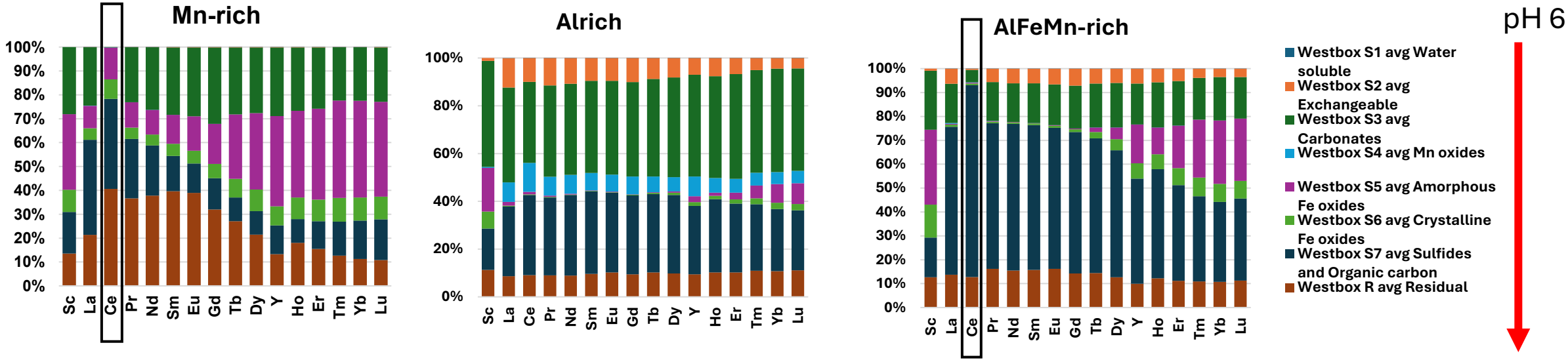
Argonne NATIONAL LABORATORY

- **AMD solids have diverse chemical composition, so extractions may need to be tailored toward different chemical compositions.**
  - 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

- Hedin, B., Stuckman, M., Lopano, C., Cravotta, C., and Capo, R. "Determination and prediction of micro scale rare earth element geochemical associations in mine drainage treatment wastes" Chemosphere. https://doi.org/10.1016/j.chemosphere.2023.140475
- Miller, J.D., Stuckman, M.Y., Means, N., Lopano, C.L., and Hakala, J.A. (2022) "Determination of transition metal ions in fossil fuel associated wastewaters using chelation ion chromatography" *Journal of Chromatography A*, 1668, 462924. https://doi.org/10.1016/j.chroma.2022.462924
- Stuckman, M., Lopano, C.L., and Tarka, T. (2022) "Step Leaching Process of Rare Earth Elements from Ash Materials Using Mild Inorganic Acids at Ambient Conditions", *U.S. Patent: US 2022/0017992 A1*. https://patents.google.com/patent/US20220017992A1/en
- Fritz, A. G., et al. (2021). "Technoeconomic Assessment of a Sequential Step-Leaching Process for Rare Earth Element Extraction from Acid Mine Drainage Precipitates." *ACS Sustainable Chemistry & Engineering* 9(28): 9308-9316.
- Hedin, B. C., et al. (2020). "Critical metal recovery potential of Appalachian acid mine drainage treatment solids." *International Journal of Coal Geology* 231: 103610.
- Hedin, B. C., et al. (2019). "The evaluation of critical rare earth element (REE) enriched treatment solids from coal mine drainage passive treatment systems." *International Journal of Coal Geology* 208: 54-64.

Ce speciation and extractabilities

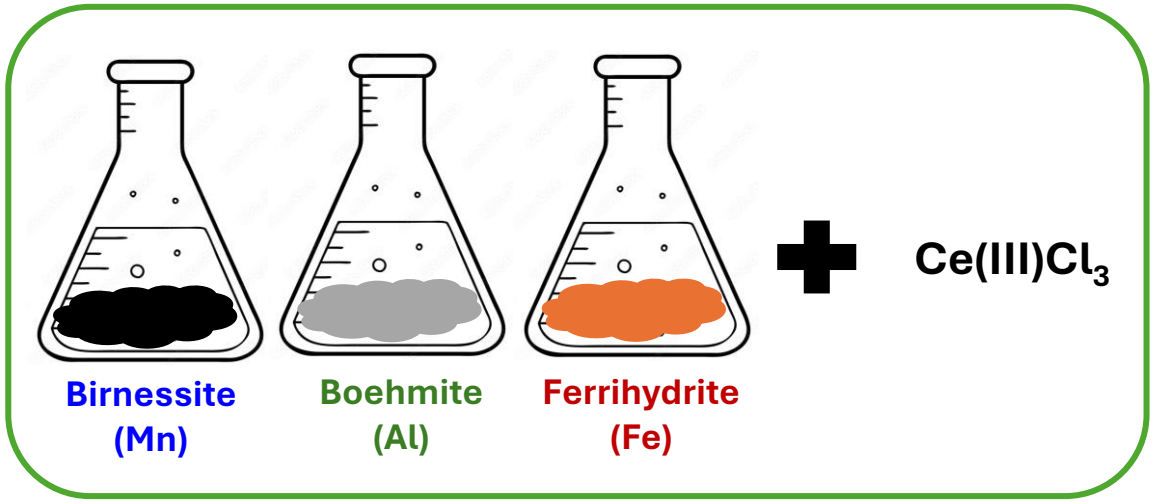
- **Ce anomalies** during sequential extraction (steps 1-3 pH 5)in Mn-rich solid and AlFeMn-rich
- **Hypothesis:**
- Ce bonding on hosting minerals are different from other REEs
- Ce redox: Ce(III) vs. Ce(IV)



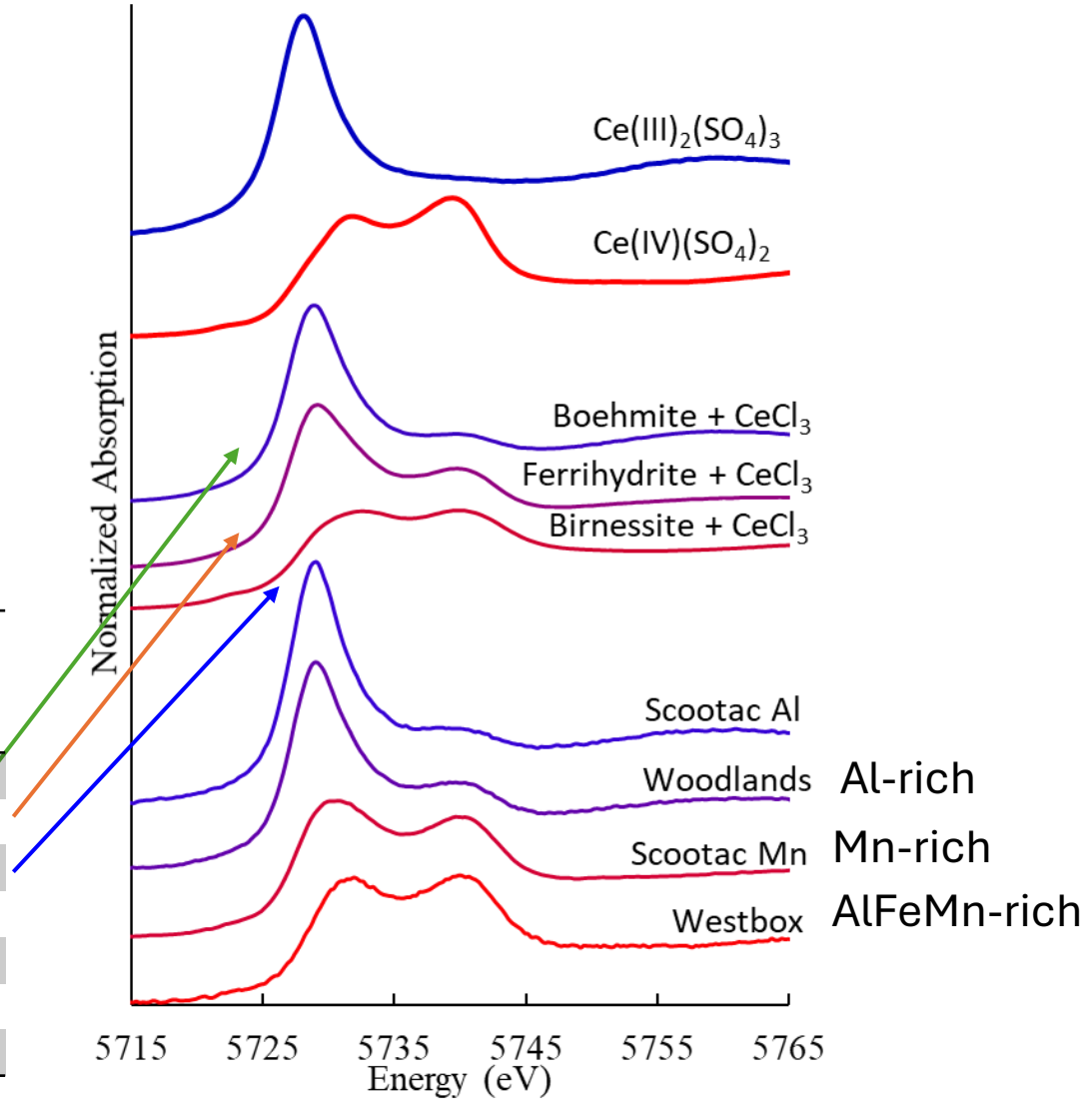
Stuckman et al., in prep, 2026

Ce oxidation varied in Al/Fe/Mn (hydr)oxides

Different Ce oxidation based on model Al/Fe/Mn (hydr)oxides



Site	Absorbed Ce loading (mmol/g)	%Ce(IV)*	%Ce(III)*	Sum	R-factor
Boehmite + $CeCl_3$	1.25	17.5 ± 0.8	82.5 ± 0.75	1.02	1.29 e-4
Ferrihydrite + $CeCl_3$	1.38	45.2 ± 0.3	54.8 ± 0.3	1.05	1.27 e-3
Birnessite + $CeCl_3$	**7.55**	**94.4 ± 0.4**	5.6 ± 0.4	0.87	1.11 e-2
$Woodlands_{(Al\text{-}rich)}$	2.06	**33.4 ± 0.5**	66.6 ± 0.5	1.07	3.79 e-3
$Scootac\text{-}Al_{(Al\text{-}rich)}$	2.08	**16.5 ± 0.6**	83.5 ± 0.7	1.09	4.98 e-3
$Scootac\text{-}Mn_{(Mn\text{-}rich)}$	1.96	**72.8 ± 0.4**	27.2 ± 0.3	1.03	2.52 e-3
$Westbox_{(Al,\ Mn,\ and\ Fe)}$	**4.26**	**87.0 ± 0.4**	13.0 ± 0.4	1.03	3.60 e-3

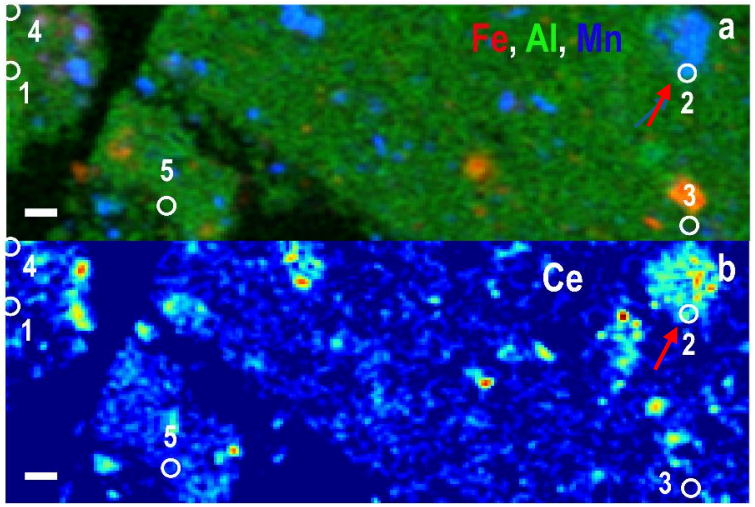


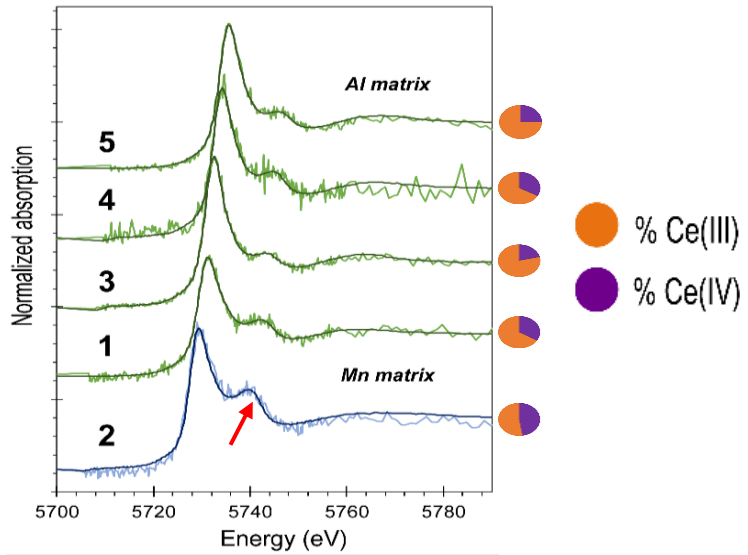
Stuckman et al., in prep, 2026

Ce oxidation increase with higher Fe/Mn

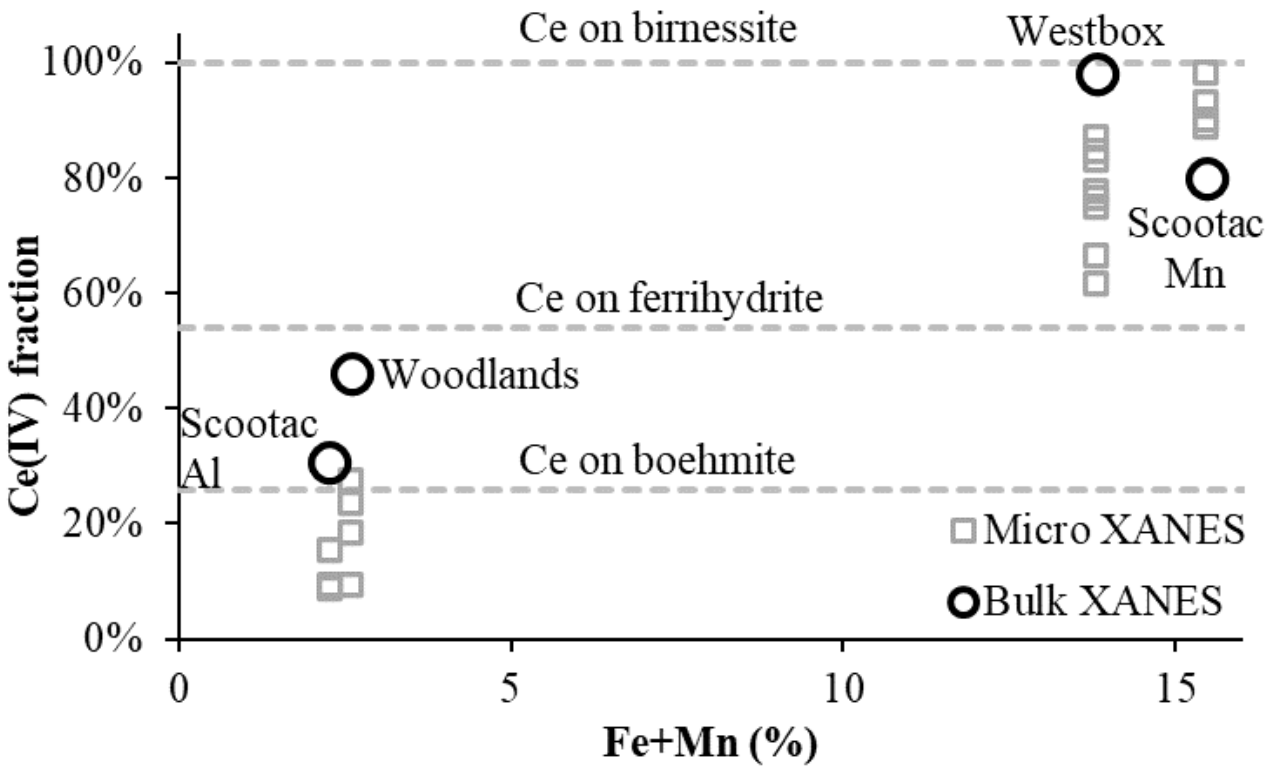
Ce oxidation in micro-Mn spots

$Scootac Al_{Al\text{-}rich}$





Ce oxidation vs. Fe+Mn contents

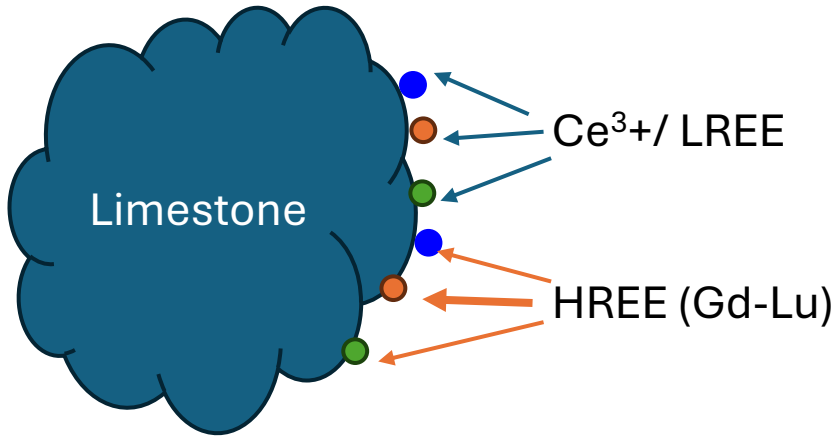


Stuckman et al., in prep, 2026

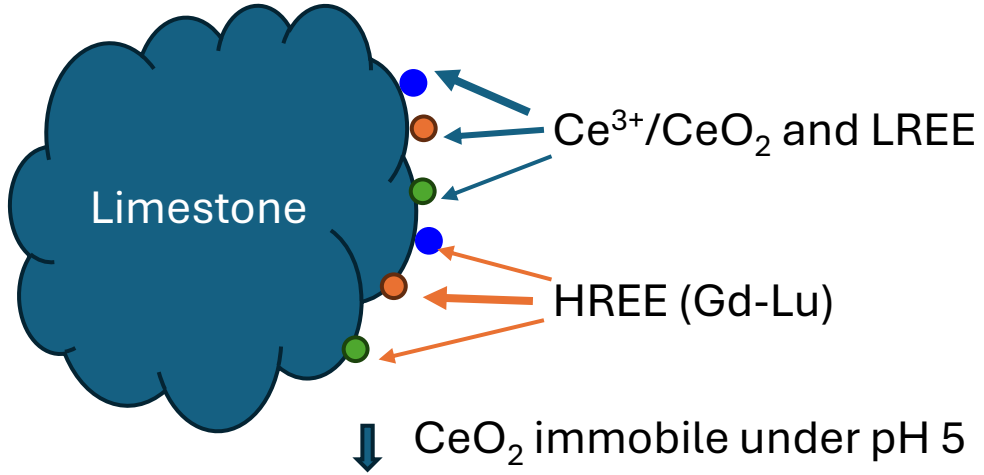
CM in Al/Mn/Fe phases: Ce oxidation and extractability

Ce oxidation observed in high Mn/Fe solids, informing extractability difference

Phase I: CM retained via Co-precipitation with Al/Mn/Fe (hydr)oxides

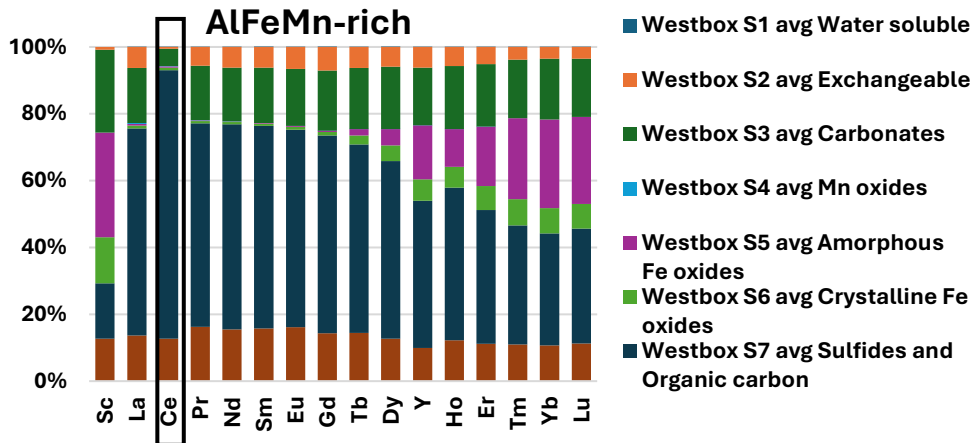


Phase II: Oxidation of CMs with Al/Mn/Fe (hydr)oxides: Ce oxidation $Ce(III)^{3+} \rightarrow Ce(IV)O_2$



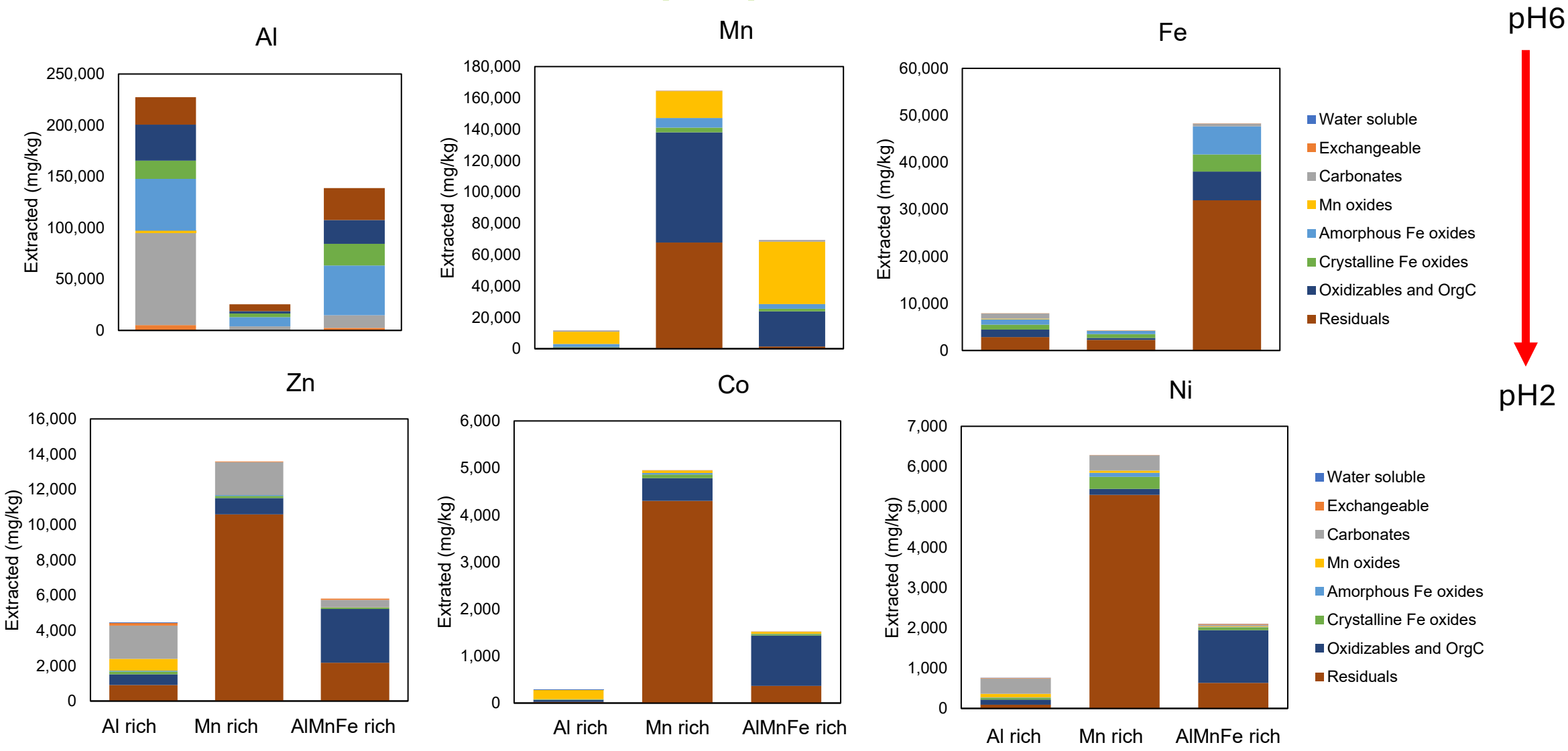
CeO_2 immobile under pH 5

- Mn (hydr)oxides, such as Birnessite (Mn)
- Fe (hydr)oxides, such as Ferrihydrite (Fe)
- Al (hydr)oxides, such as Boehmite (Al)



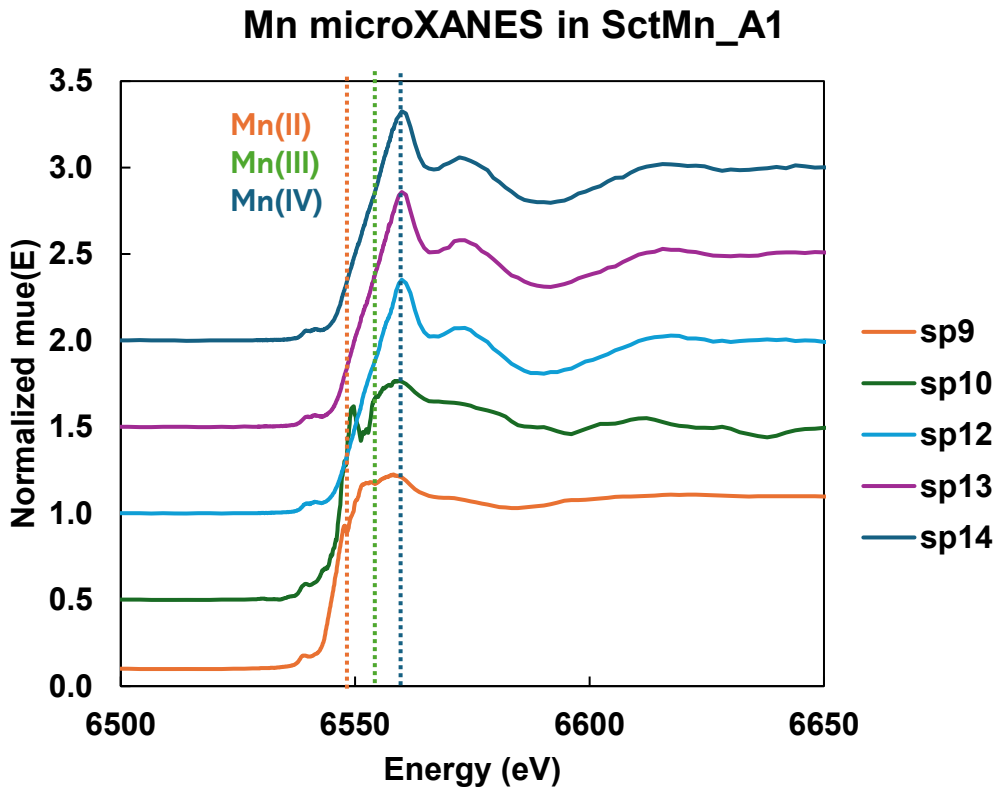
Transition Metal Fractionation and Extractability

Enriched Co in more recalcitrant Mn (hydr)oxide phase in SctMn



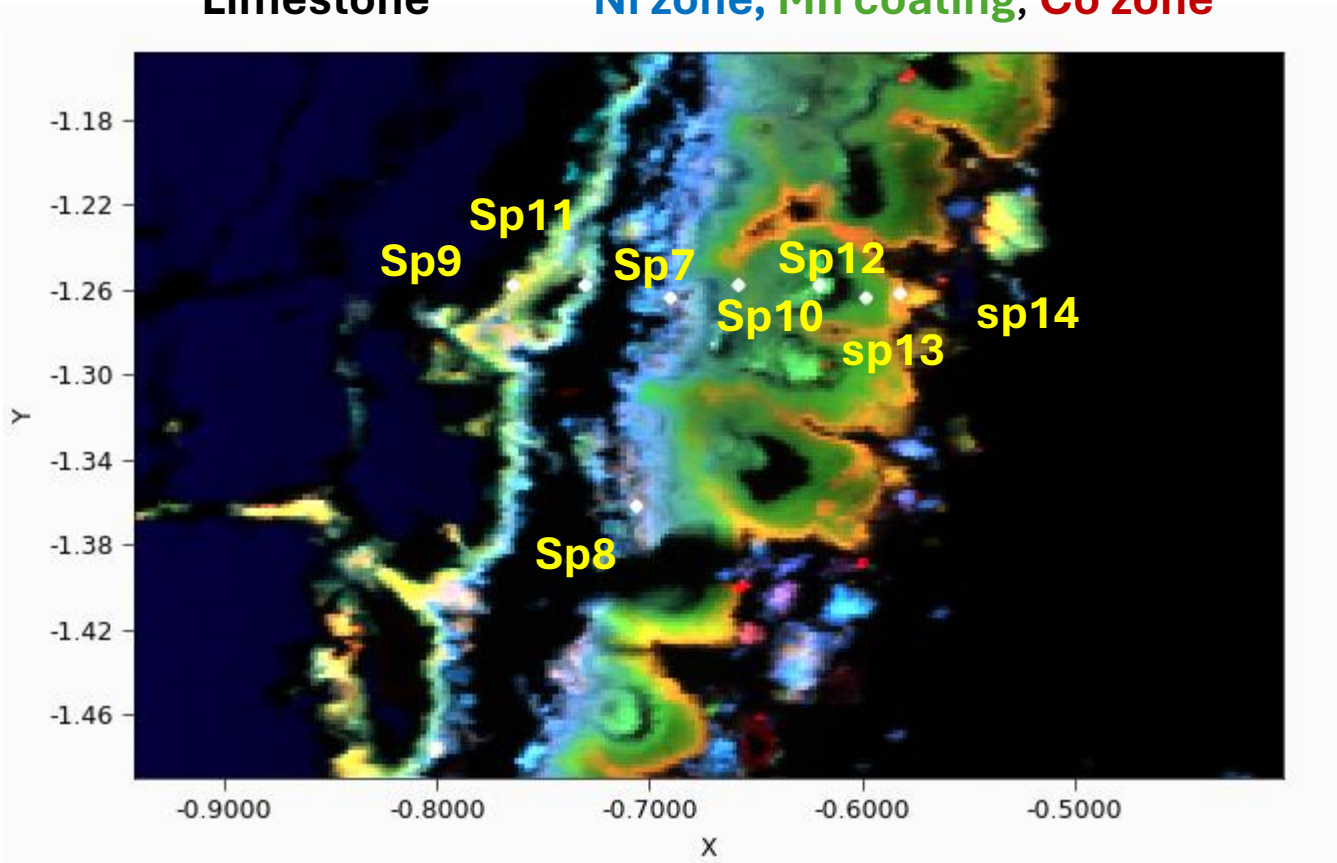
Co/Mn/Ni layered deposition in Mn-rich sample

Mn Layer: Sp9-sp14, **Mn(II), Mn(III) to Mn(IV)**



SctMn with Mn layers

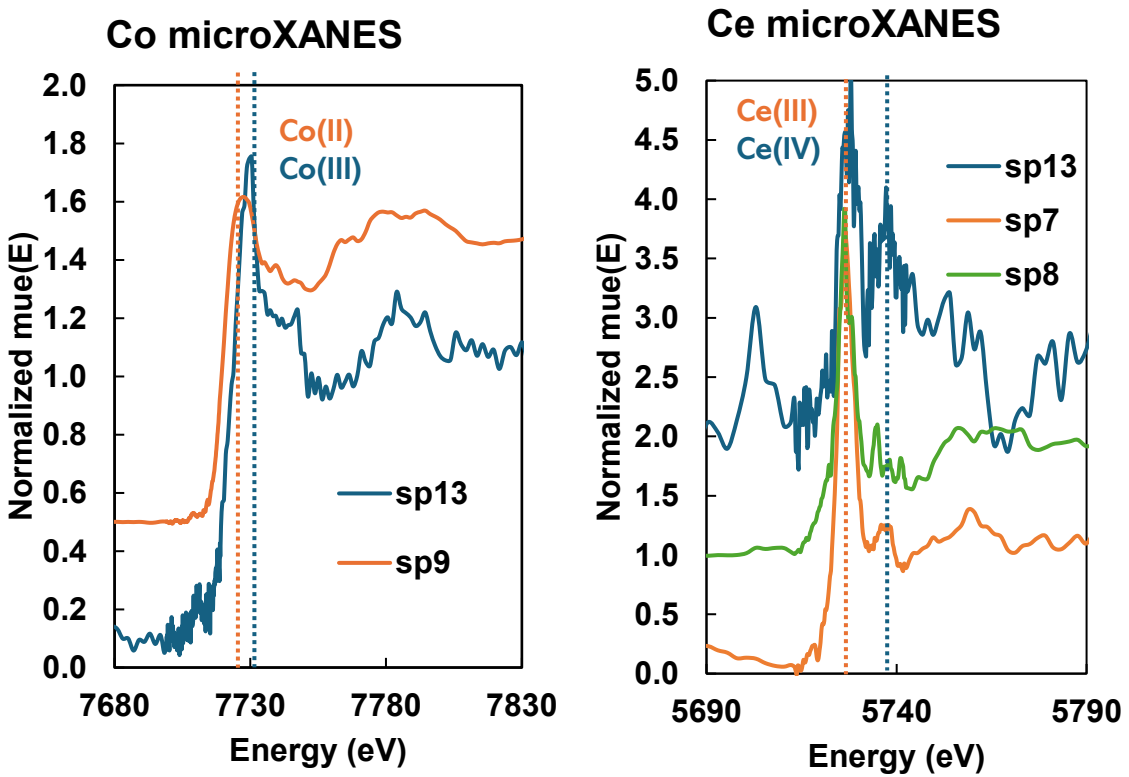
Limestone **Ni zone, Mn coating, Co zone**

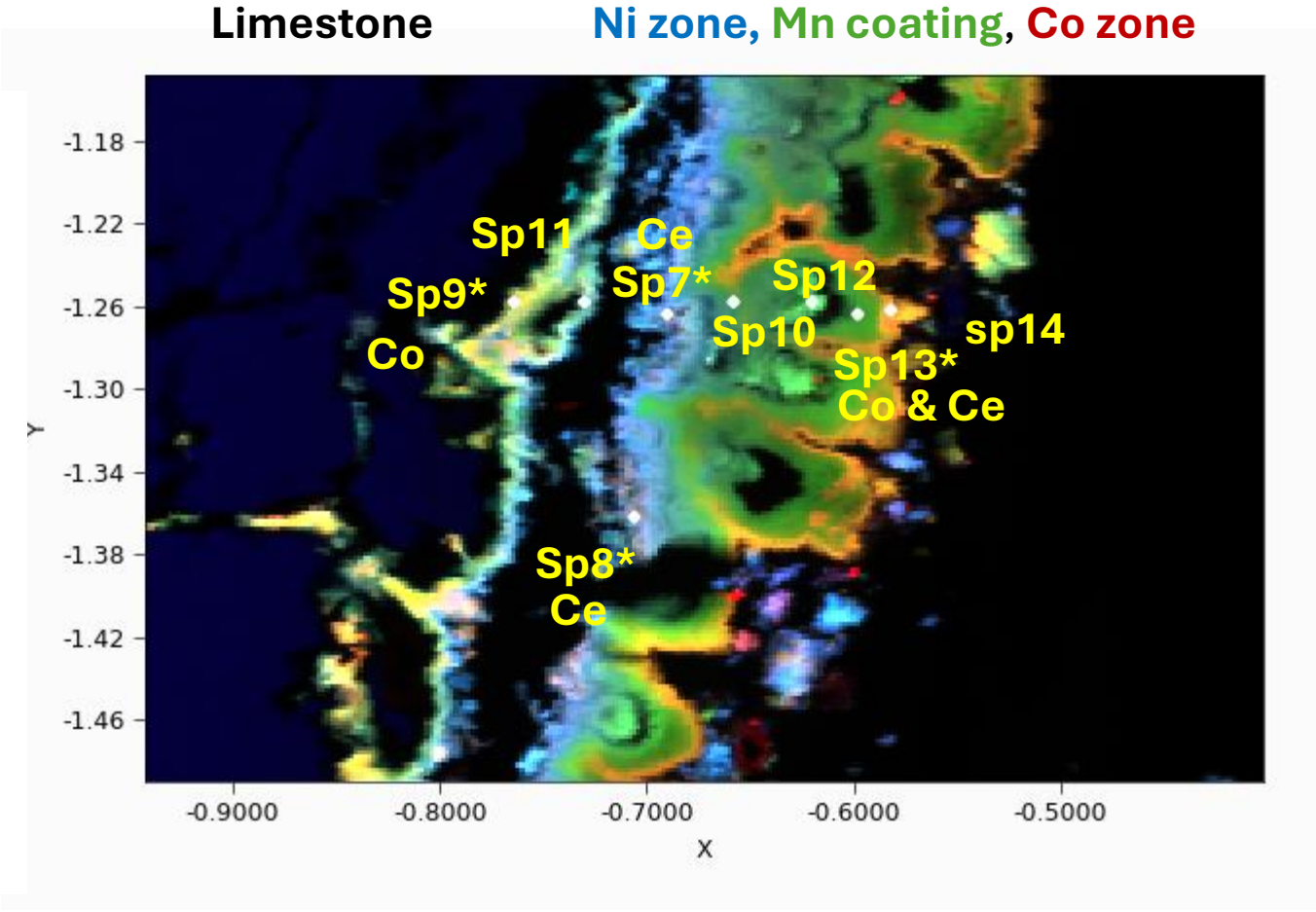


MicroXRF maps (0.5mm X 0.3mm), 2 micron/step @ 12keV

Co/Mn/Ni layered deposition in Mn-rich sample

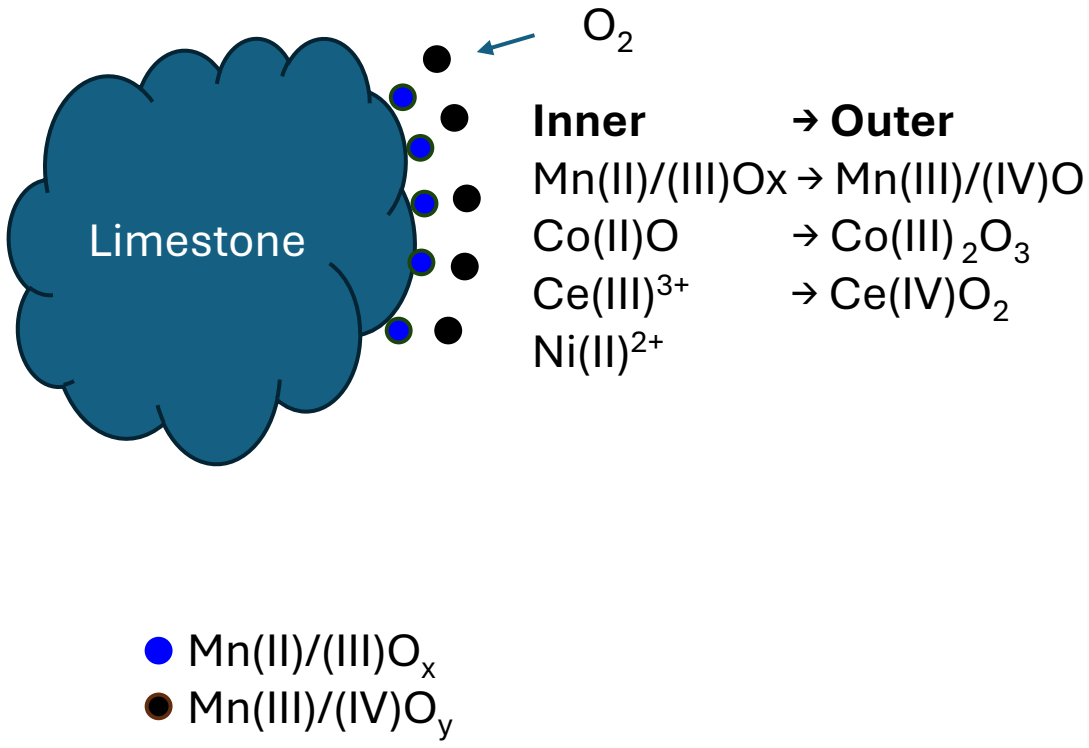
- From inner layer to outer layer:
- Co(II) to Co(III); Ce (III) to Ce(IV)



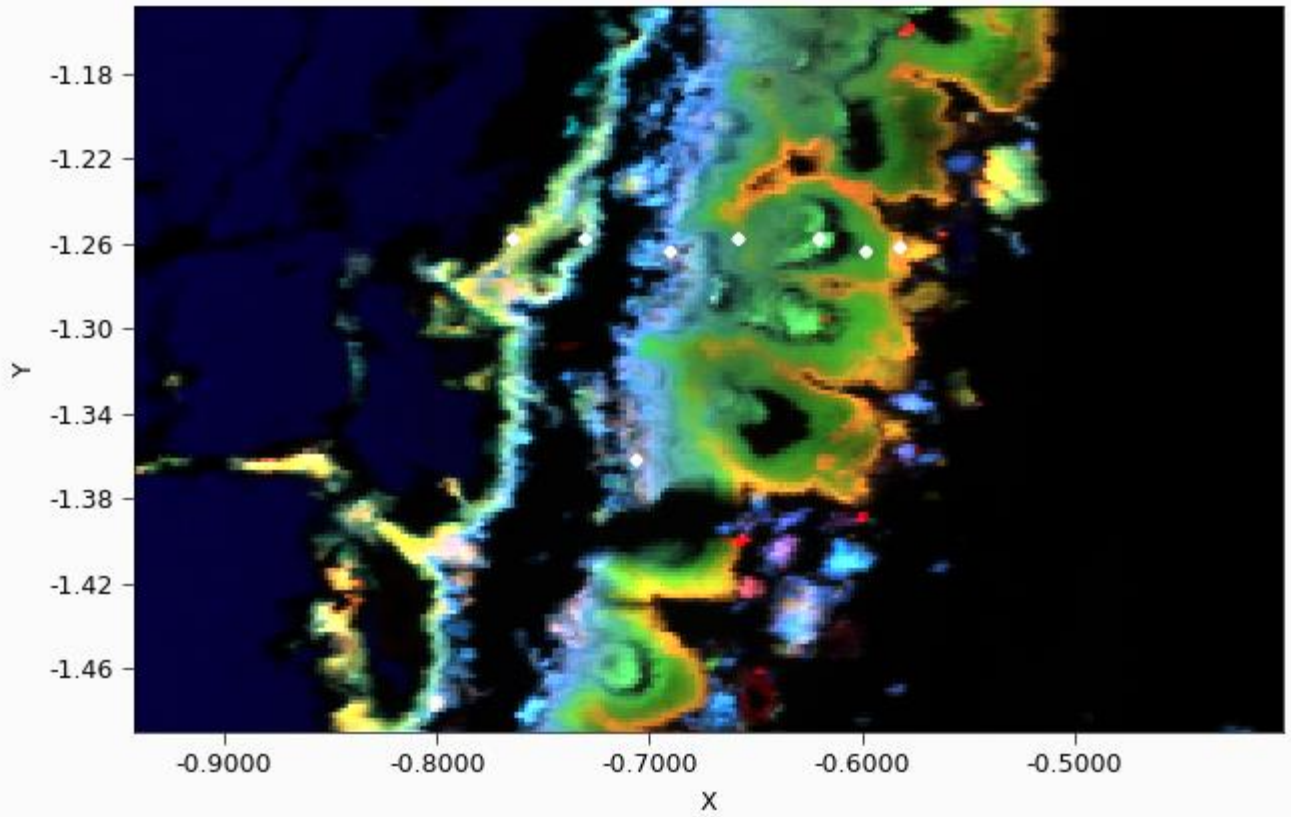


Co/Mn/Ni layered deposition in Mn-rich sample

Phase II: Oxidation of CM with Al/Mn/Fe (hydr)oxides, Co/Mn/Ce oxidation



Limestone **Ni zone, Mn coating, Co zone**

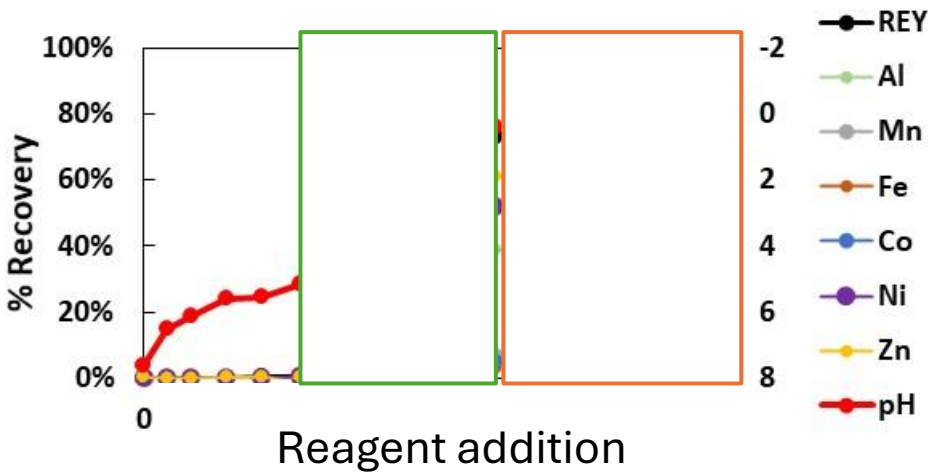


Co mobilization and sorption study on Mn (hydr)oxides

NATIONAL ENERGY TECHNOLOGY LABORATORY

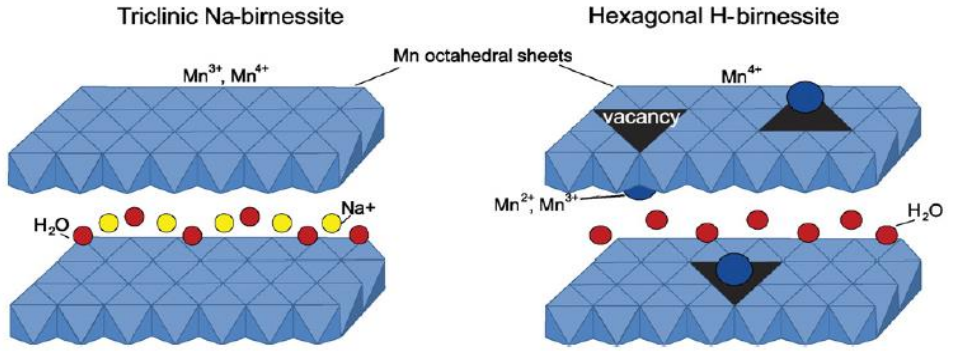
Co mobilization separate from other CMs

- REE/Al/Ni/Zn coextraction
- Co/Mn coextraction



- Shaffer et al. (in prep)
- Co sorbed onto birnessite are pH dependent (max @ pH 4.5)

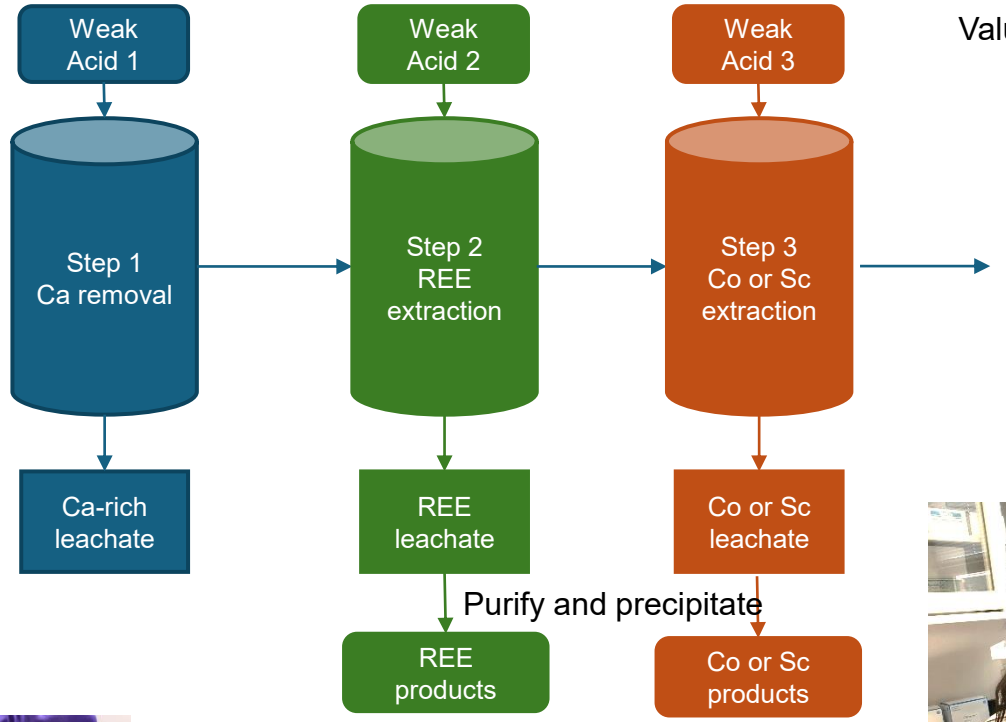
Mn-oxide Mineral	Crystal Structure	% Range in Passive Treatment Systems (Tan et al., 2010)	%Avg
Na birnessite	Triclinic	2-50	24.6
H-birnessite	Hexagonal	45-98	65.8
Todorokite	Tunnel	0-29	9.6



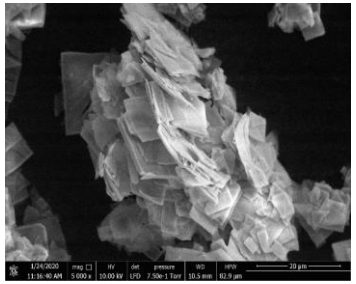
Targeted Rare Earth Extraction (TREE)

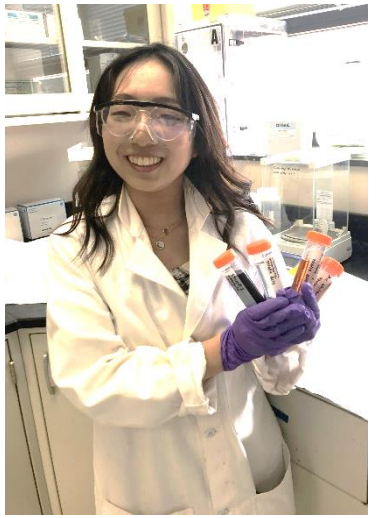
Targeting select Coal and mining wastes to Reduce Extraction Steps & Conditions

- ✓ Starting material is a waste product – no mining required
- ✓ Limited pre-processing prior to extraction: no grinding or other steps required
- ✓ No heating or elevated pressure required
- ✓ Mild acids (up to **90%** reduction in acid consumption compared to other pathways) and high REE recovery (**80-100%** recovery rate)
- ✓ Wastes with "mild" pHs limits disposal costs
- ✓ Potential for additional byproducts/value streams to further improve process economics









***Stuckman, M.Y., Lopano, C.L. and Tarka, T. (2025) U.S. Patent No.: US 12,221,672**

https://www.energy.gov/articles/energy-department-acts-unleash-american-coal-strengthening-coal-technology-and-securing

Conclusions

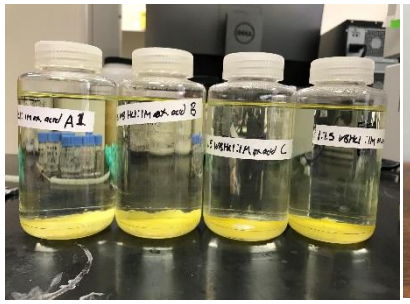
- **AMD solids have diverse chemical composition, so extractions may need to be tailored towards different chemical composition.**
  - REEs mostly co-localized with Al and Mn, selected HREEs (Gd/Dy) co-localized with Fe
  - Regardless of composition, Co, Ni, Zn mainly co-localized with Mn (hydr)oxides in AMD solids
  - Ce(IV) increases with Mn/Fe contents; Co enriched with high Mn contents in AMD solids
- **Innovative Solutions:**
- **In progress! Novel extractions informed by characterization - Stay tuned for more.**



AMD solids



Large scale leaching

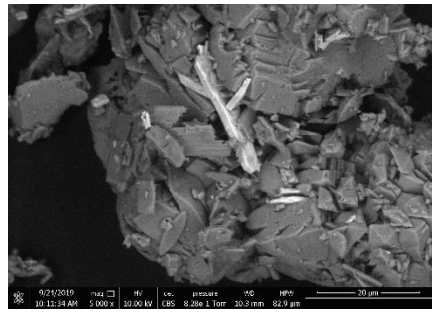


Direct oxalic acid precipitation



Oxalates

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



SEM image of REE oxalates in end product

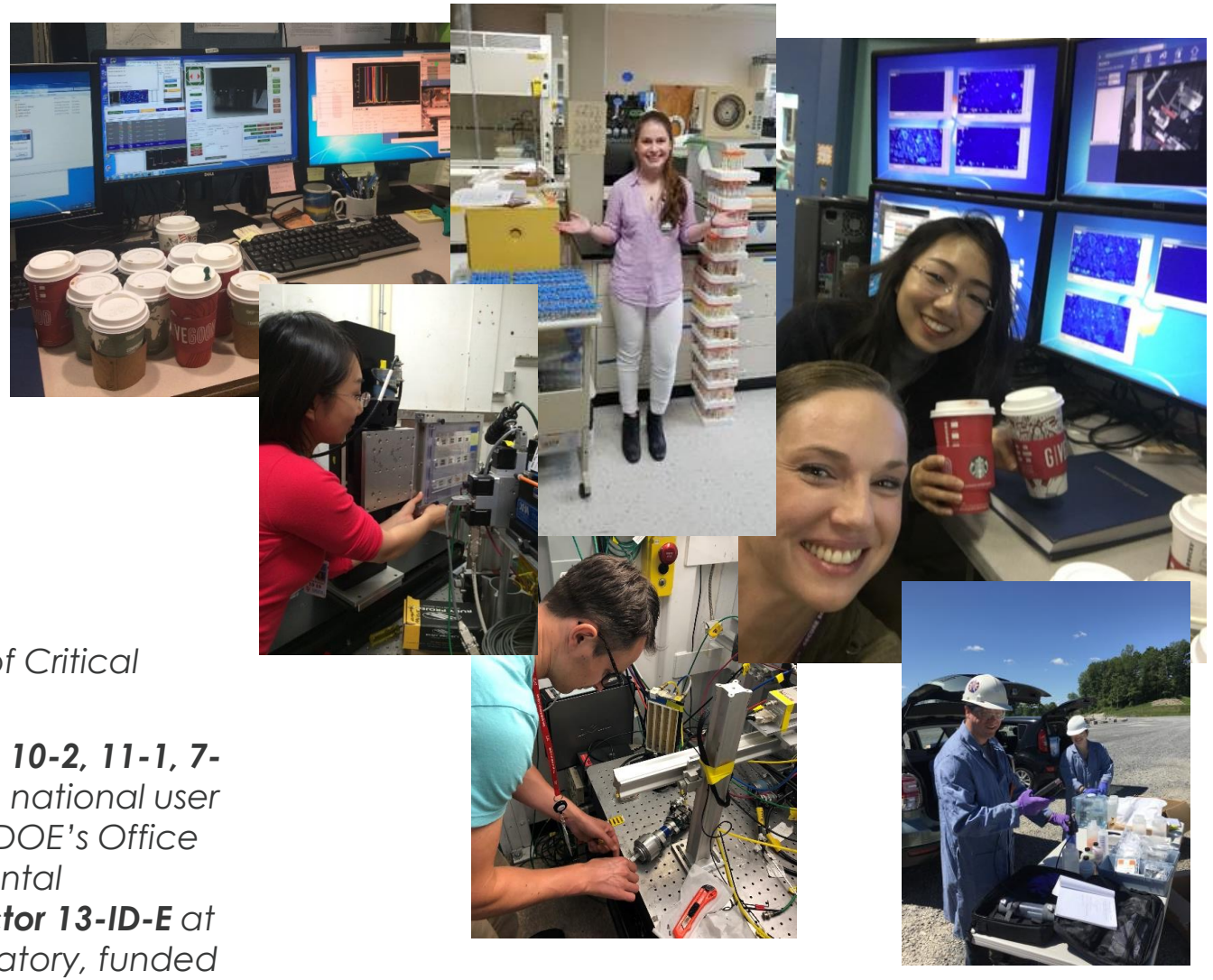
Acknowledgements

- **Coffee….Lots of Coffee**

- Hedin Environmental, LLC
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- Dr. Matt Newville, Dr. Antonio Lanzirotti (APS)

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Opportunities

- **NETL is hiring**
- NETL is hiring a cohort to research critical mineral and materials from domestic sources (ORISE fellowship)
- https://netl.doe.gov/sites/default/files/2024-09/Intern%20Postdoc%20Cohort_Template%20R4_Digitial.pdf

Student Internship



Post-graduates



- Mickey Leland Intern Program (MLEF)
- https://orise.orau.gov/mlef/

- **NETL is hiring**
- **CM processing for Fines and Slimes**
  - Experimentalist (physical separation and advanced characterization)
  - Modeler
- **Mine of Future: CM recovery from in-situ recovery of sedimentary rock formations**
  - Student interns

- Mengling.stuckman@netl.doe.gov

Thank you!

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@NationalEnergyTechnologyLaboratory

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National Energy Technology Laboratory

Center of Excellence for Critical Minerals and Advanced Alloys

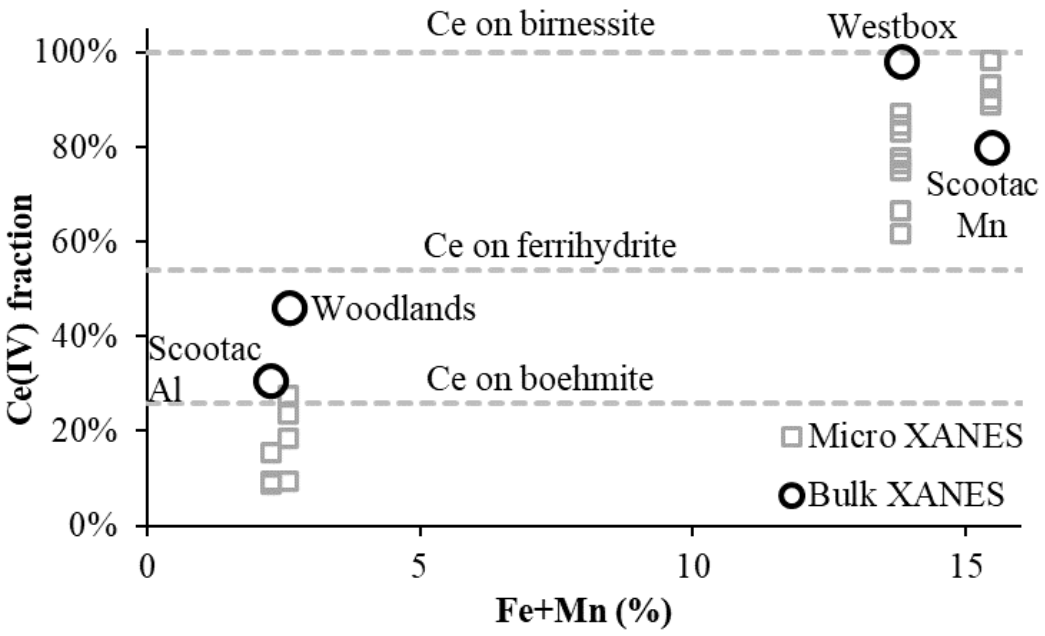
criticalminerals@netl.doe.gov

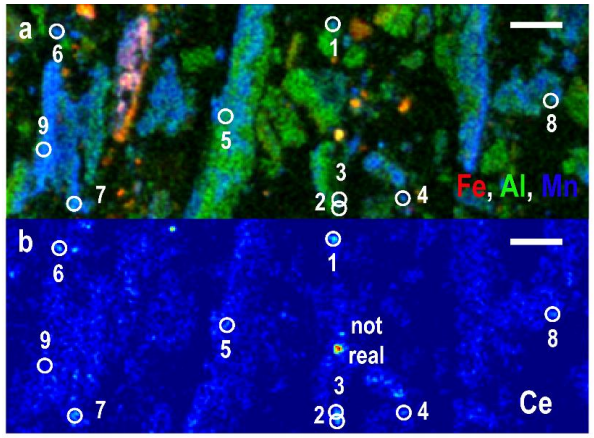
Ce oxidation based on %Fe/Mn in AMD solids

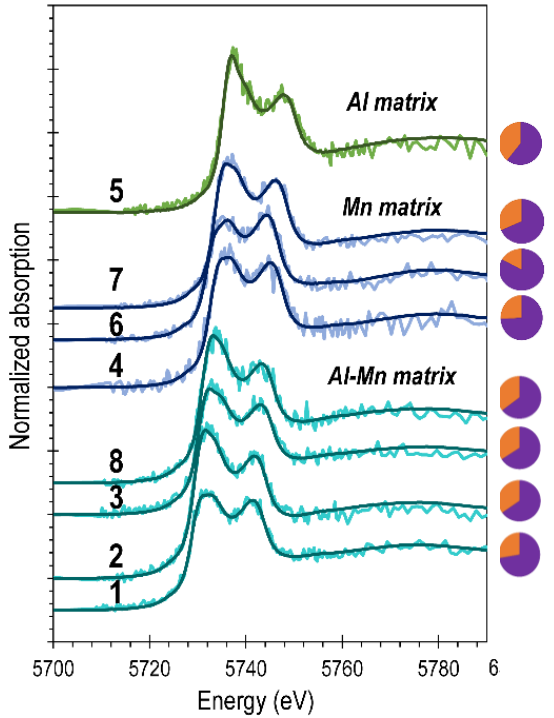
bulk Ce XANES and micro-XANES analysis

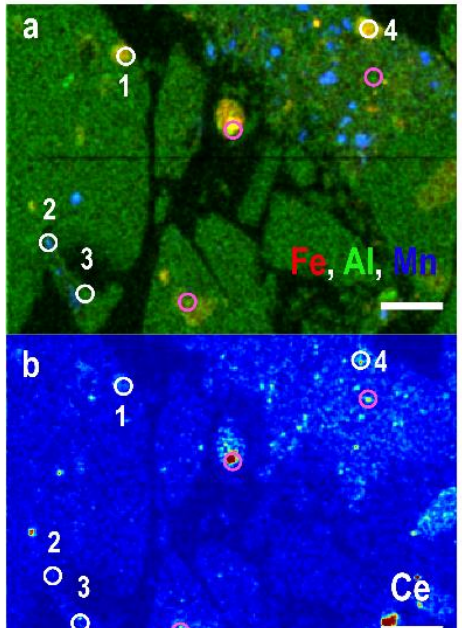
Stuckman et al., in prep, 2026

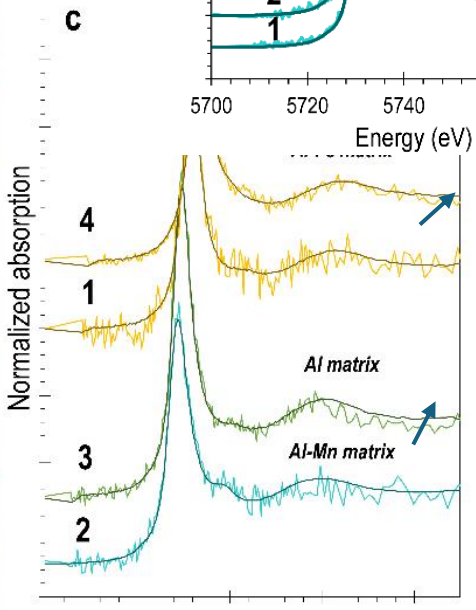
- %Ce(IV) increases with higher Fe/Mn phases, resulting in extractability anomaly in mild pH ranges
- Implication: Ce separation







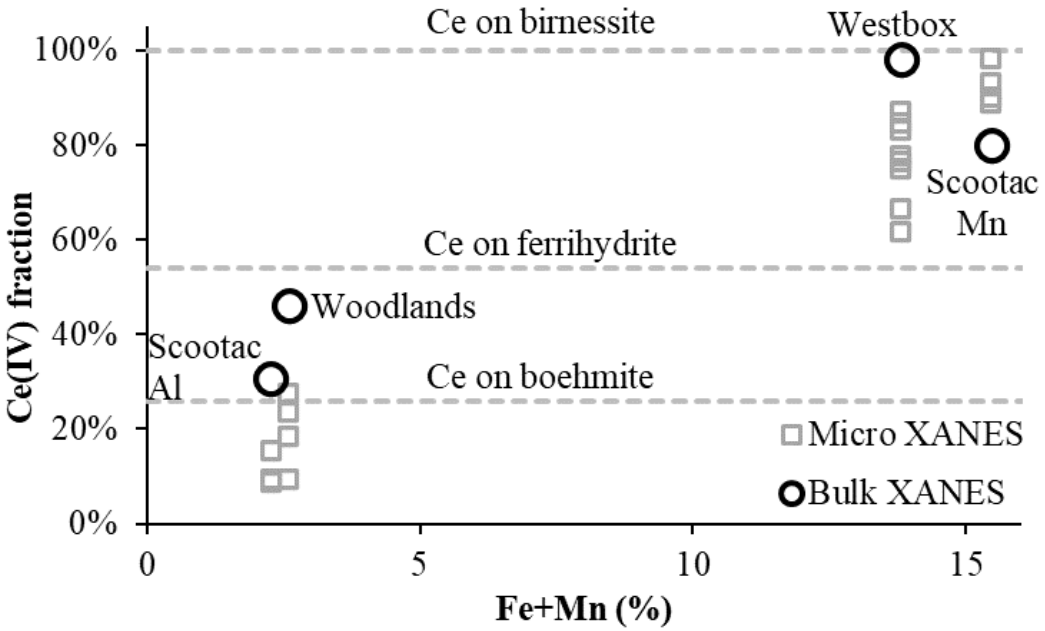




Ce oxidation based on %Fe/Mn in AMD solids

bulk Ce XANES and micro-XANES analysis

- %Ce(IV) increases with higher Fe/Mn phases in both micro-environments and bulk environments, resulting in extractability anomaly in mild pH ranges



Stuckman et al., in prep, 2026

