

# ELECTRO-ASSISTED EXTRACTION OF CRITICAL RAW MATERIALS FROM COAL ASH

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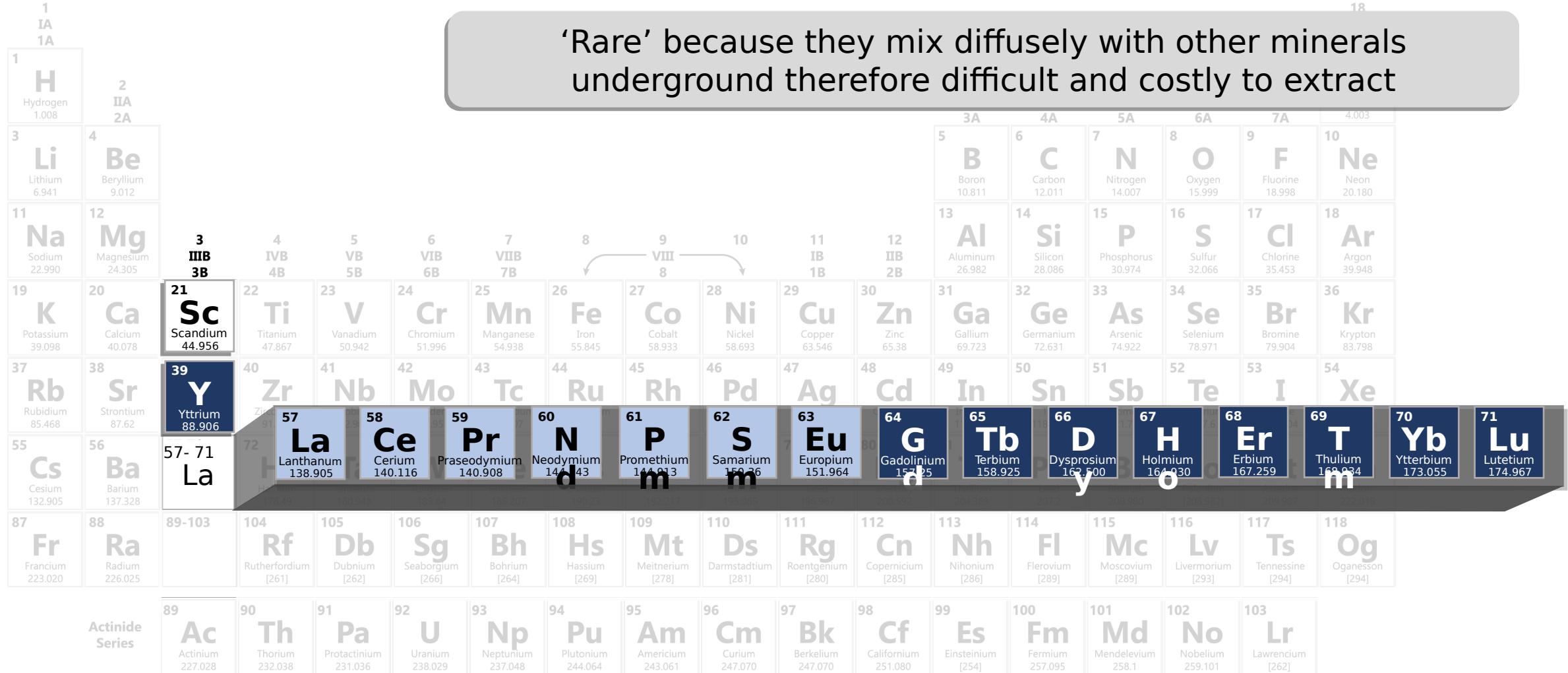
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# Rare Earth Elements (REEs)

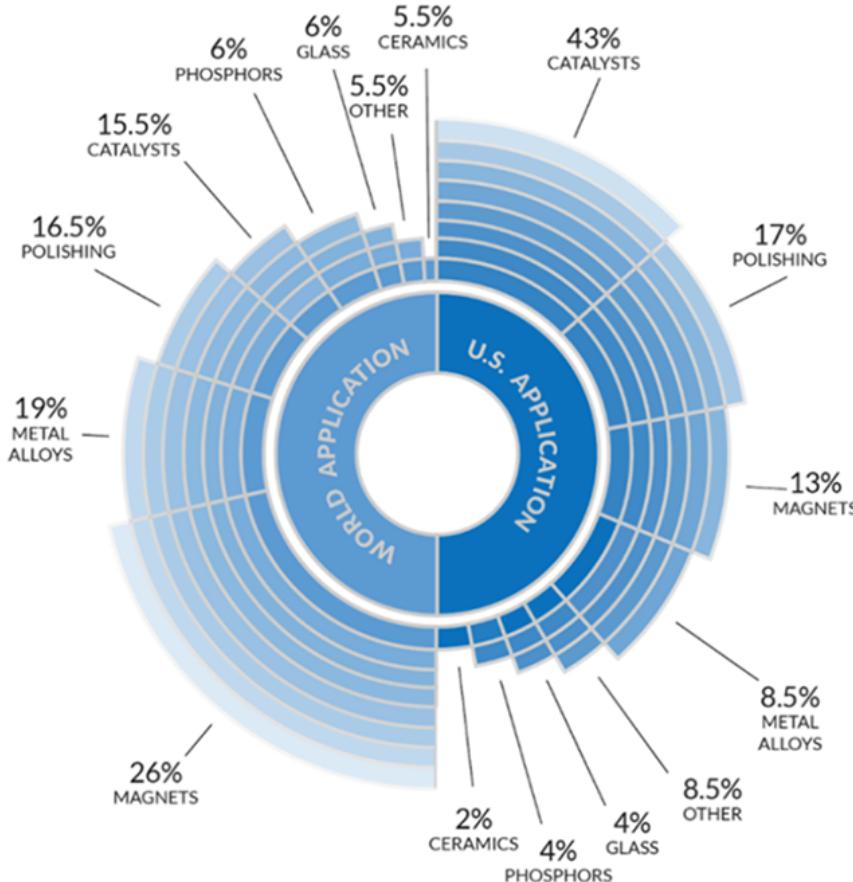
'Rare' because they mix diffusely with other minerals  
underground therefore difficult and costly to extract



The Periodic Table of Elements is shown, highlighting the Rare Earth Elements (REEs). The REEs are grouped into two main blocks: the Lanthanide series (lanthanum to lutetium) and the Actinide series (actinium to lawrencium). These elements are characterized by their similar chemical properties due to their close atomic numbers and electron configurations.

1 IA 1A	H Hydrogen 1.008	2 IIA 2A	Be Beryllium 9.012	3 3 IIIIB 3B	Li Lithium 6.941	4 IVB 4B	Sc Scandium 44.956	5 VB 5B	V Vanadium 50.942	6 VIB 6B	Cr Chromium 51.996	7 VIIIB 7B	Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798	18						
11 Na Sodium 22.990	12 Mg Magnesium 24.305	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798	10 Ne Neon 20.180	4.003												
19 K Potassium 39.098	20 Ca Calcium 40.078	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 95.94	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.46	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.33													
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 95.94	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.46	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.33														
55 Cs Cesium 132.905	56 Ba Barium 137.328	57- 71 La Lanthanum 138.905	57 La Lanthanum 138.905	58 Ce Cerium 140.116	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.943	60 Nd Neodymium 144.943	61 Pm Promethium 144.913	61 Pm Promethium 144.913	62 Sm Samarium 150.26	62 Sm Samarium 150.26	63 Eu Europium 151.964	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	67 Ho Holmium 164.930	68 Er Erbium 167.259	68 Er Erbium 167.259	69 Tm Thulium 168.934	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967	71 Lu Lutetium 174.967
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessee [294]	118 Og Oganesson [294]														
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]																

# REEs applications



## MAGNETICS

Computer Hard Drives  
 Disk Drive Motors  
 Anti-Lock Brakes  
 Automotive Parts  
 Frictionless Bearings  
 Magnetic Refrigeration  
 Microwave Power Tubes  
 Power Generation  
 Microphones & Speakers  
 Communication Systems  
 MRI



## METAL ALLOYS

NiMH Batteries  
 Fuel Cells  
 Steel  
 Super Alloys  
 Aluminum/Magnesium



## DEFENSE

Satellite Communications  
 Guidance Systems  
 Aircraft Structures  
 Fly-by-Wire  
 Smart Missiles



## CATALYSTS

Petroleum Refining  
 Catalytic Converter  
 Fuel Additives  
 Chemical Processing  
 Air Pollution Controls



## CERAMICS

Capacitors  
 Sensors  
 Colorants  
 Scintillators  
 Refractories



## PHOSPHORS

Display phosphors-  
 CRT,LPD,LCD  
 Fluorescents  
 Medical Imaging  
 Lasers  
 Fiber Optics



## GLASS & POLISHING

Polishing Compounds  
 Pigments & Coatings  
 UV Resistant Glass  
 Photo-Optical Glass  
 X-Ray Imaging

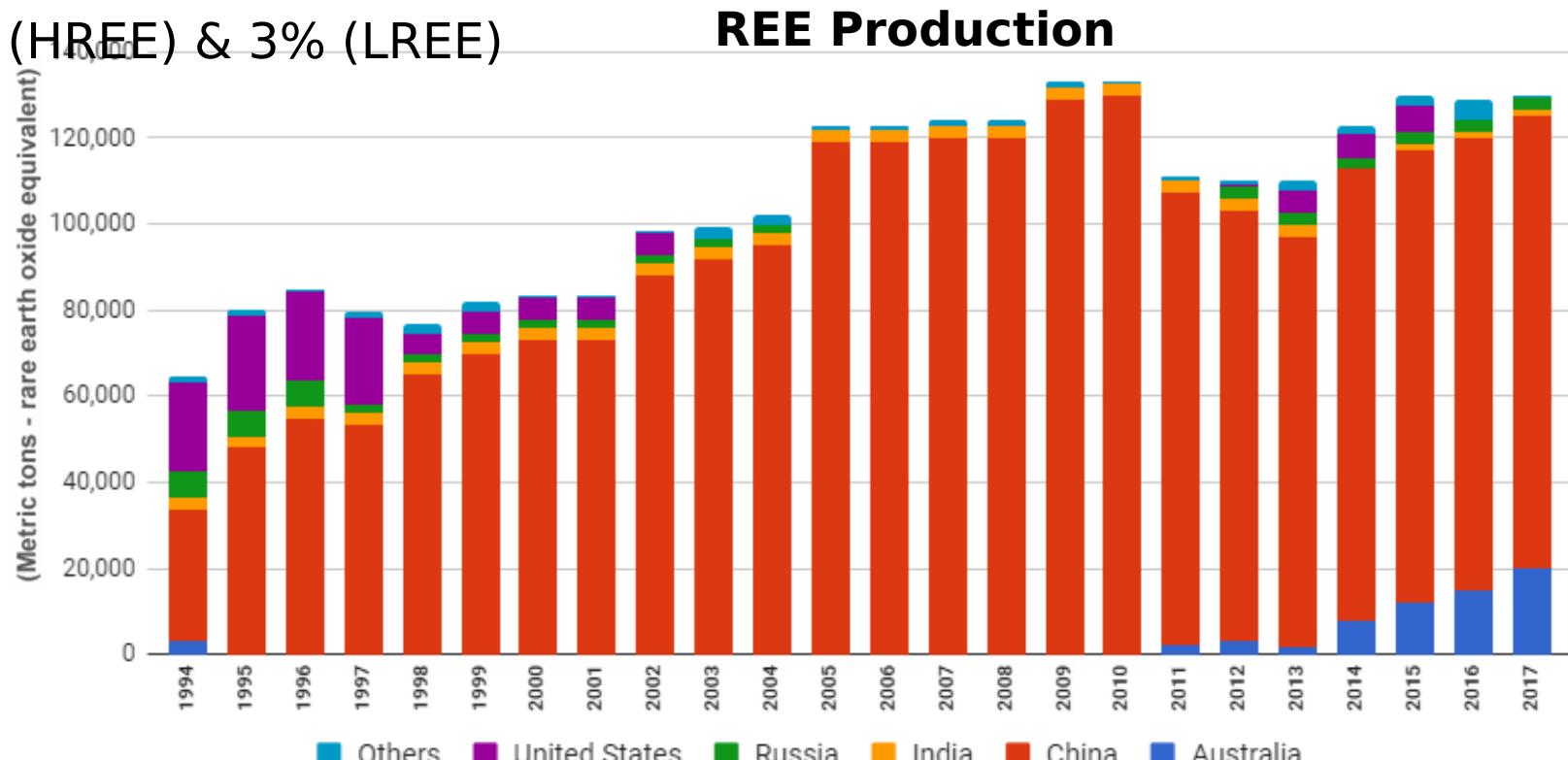


# Problem

## EU overview

- o EU is almost entirely dependent upon imports from China
- o The 2011 REE-price crisis pointed to the need to reduce the dependence on China's imports
- o Substitution Index\*\*: 0.96 (HREE) & 0.91 (LREE)
- o End of life recycling rate: 8% (HREE) & 3% (LREE)

1



\*\* 0 - 1: 1 means non-substitutable

1  
EU, 2017

Source: Geology.com using data from the

# Geopolitical strategy



UNITED STATES  
OF AMERICA

Final List of 35 Minerals deemed critical to U.S. National Security and Economy

2018 May (Dep. of Interior)



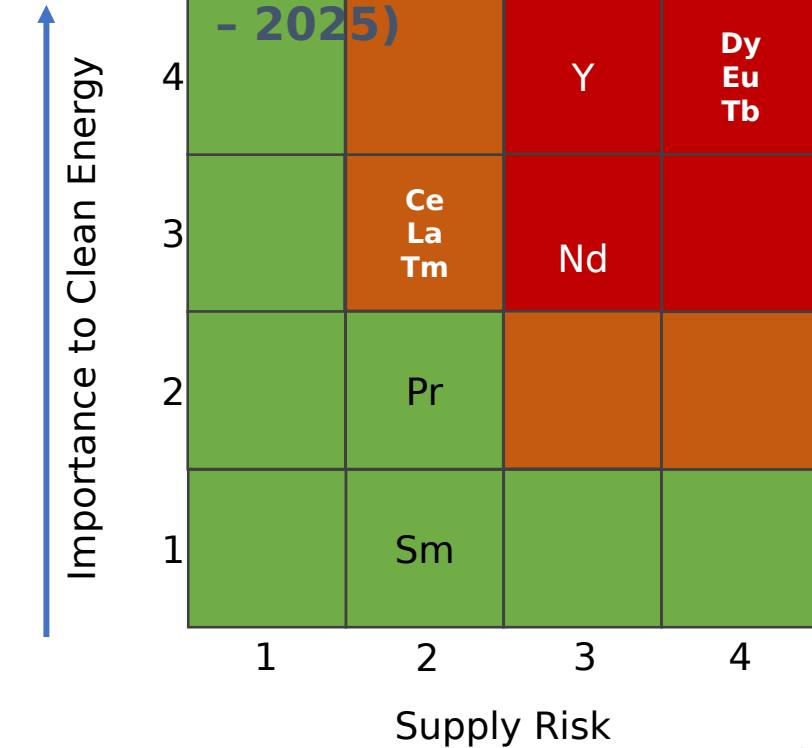
European Union

List of Critical Raw Materials for the EU – 27 CRMs

2017 September (European Commission)

- 2011 *Critical Materials Strategy* - by the U.S. Department of Energy - includes criticality assessments:

- Supply challenges for 5 REE may affect clean energy technology deployment in the years ahead.



# Aim

Recovery of REEs from a **secondary resource** (e.g. coal by-product) through electro-based technologies

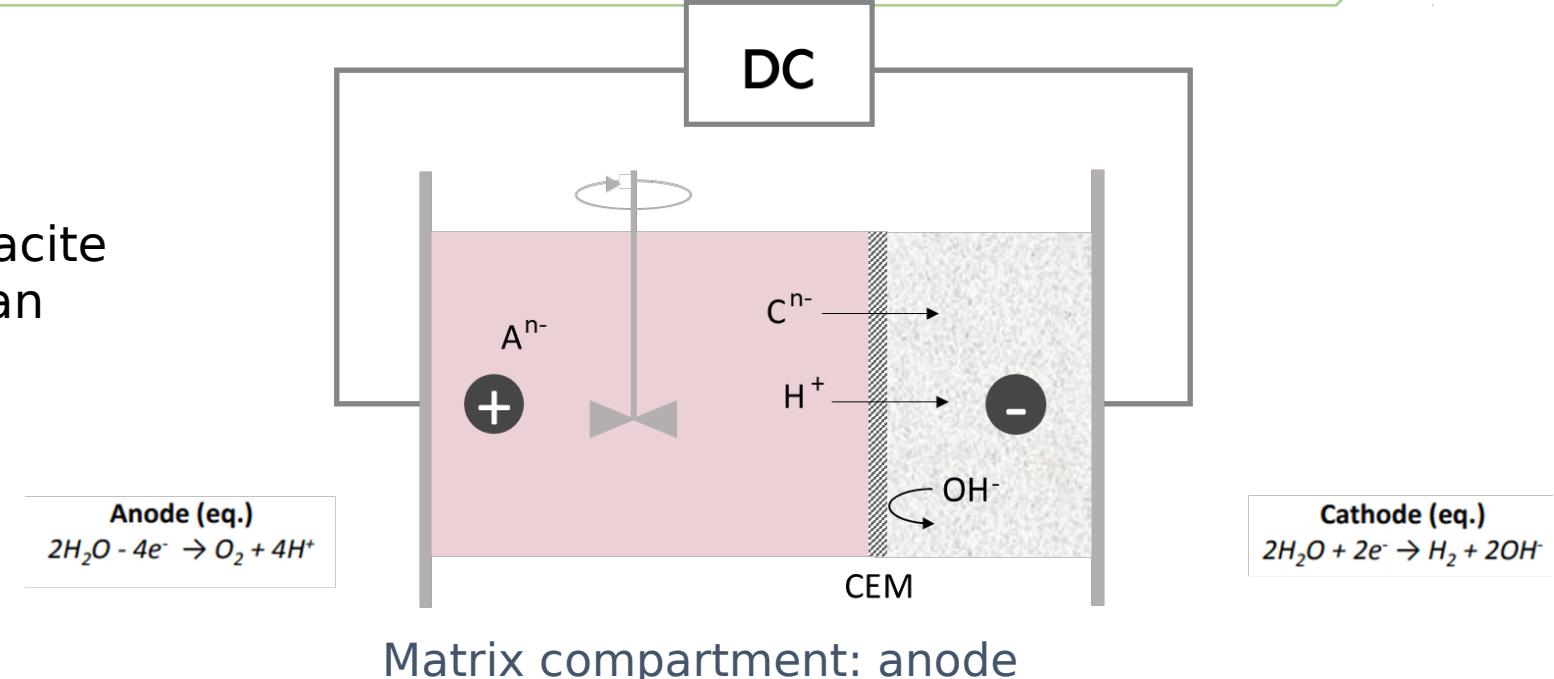
Efficient & environmentally-friendly separation and processing technology

In progress:

- Assessment and analysis of the feasibility of **electrodialytic recover of REEs from anthracite ash**
- Proof of concept**

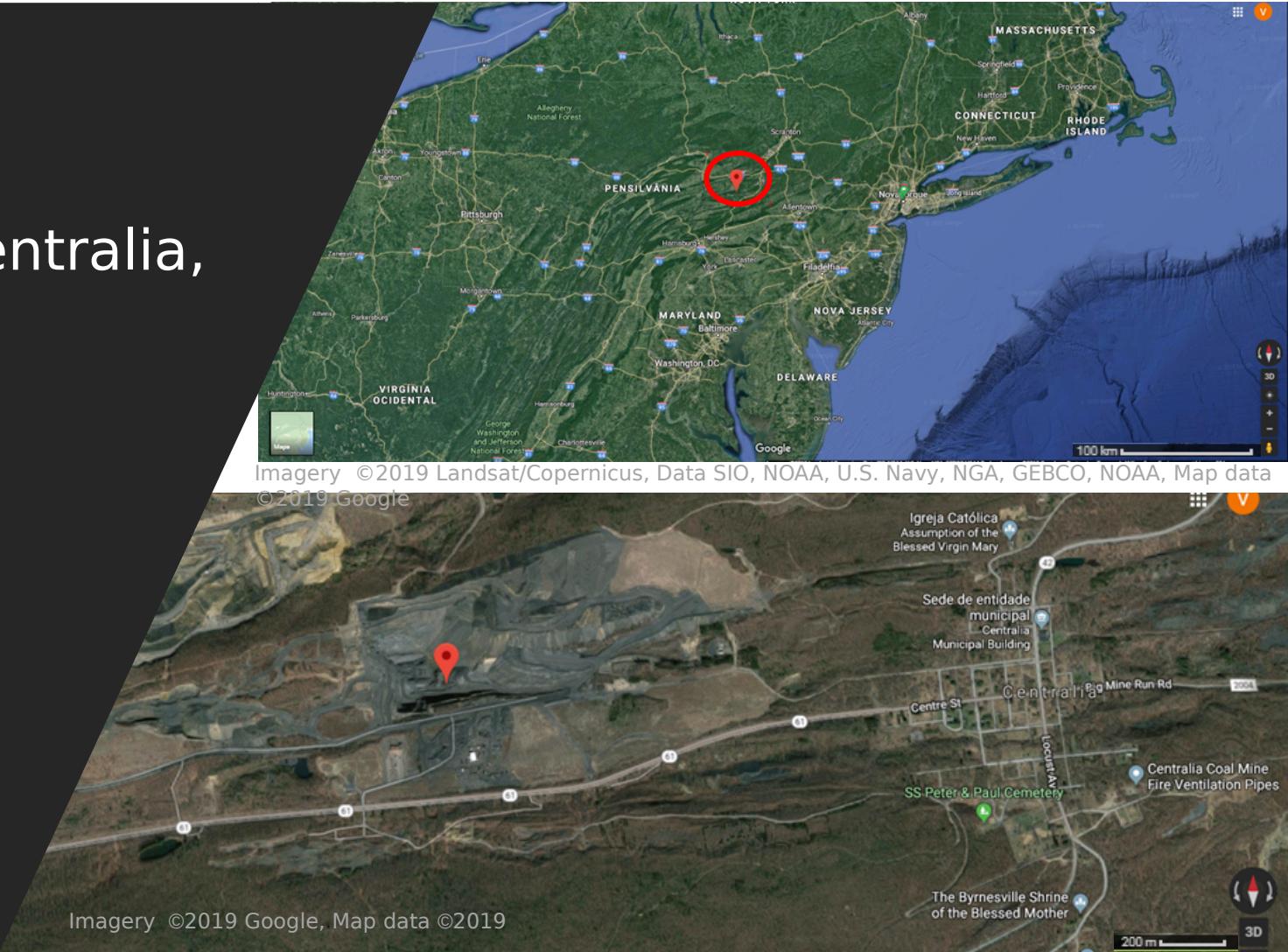
## Electrodialytic Process

Recover of REEs from fine anthracite coal ash under the influence of an applied low level direct current

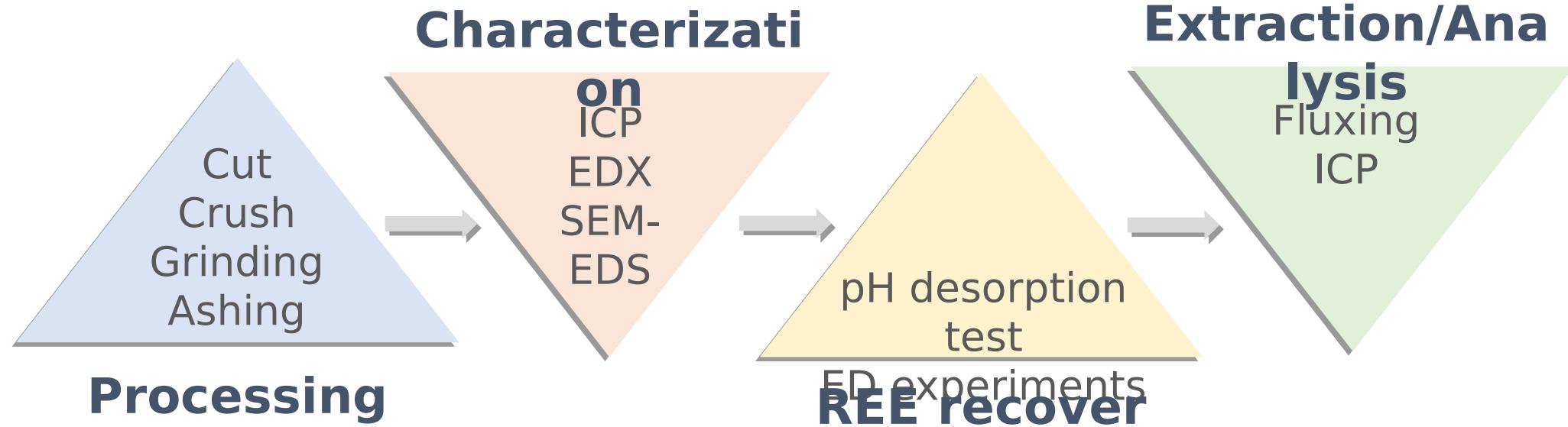


# Anthracite origin

- Blaschak Coal Corporation, Centralia, PA, USA
- Northern Pennsylvania
  - Lat. 40.8° N, Long. 76.36° W
- **Mammoth Vein**



# Methodology



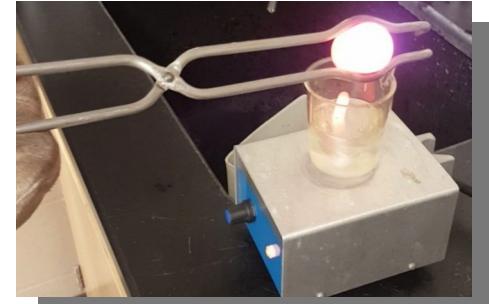
**Anthracite**



**Anthracite ash  
ASTM (D3174-12)**



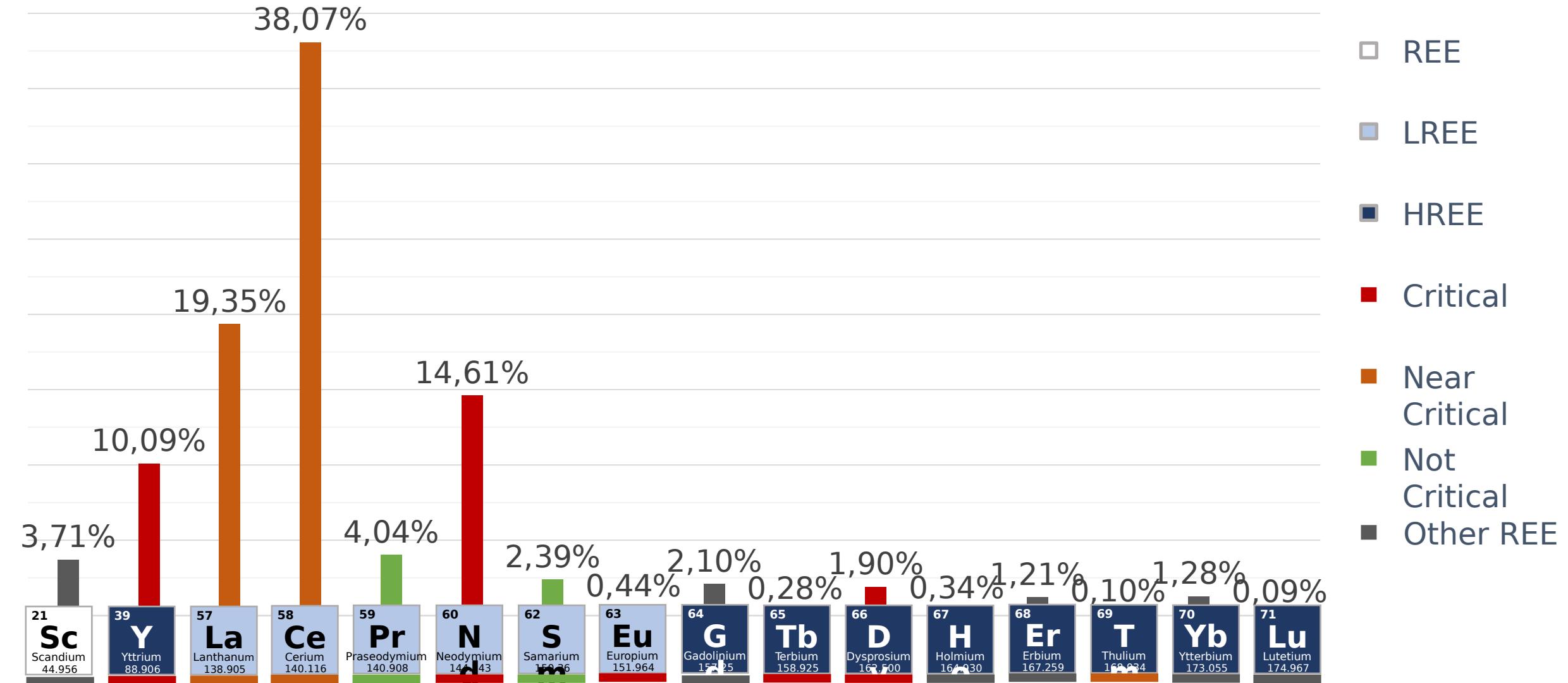
**Electrodialytic cell**



**Fluxing**

# Characterization

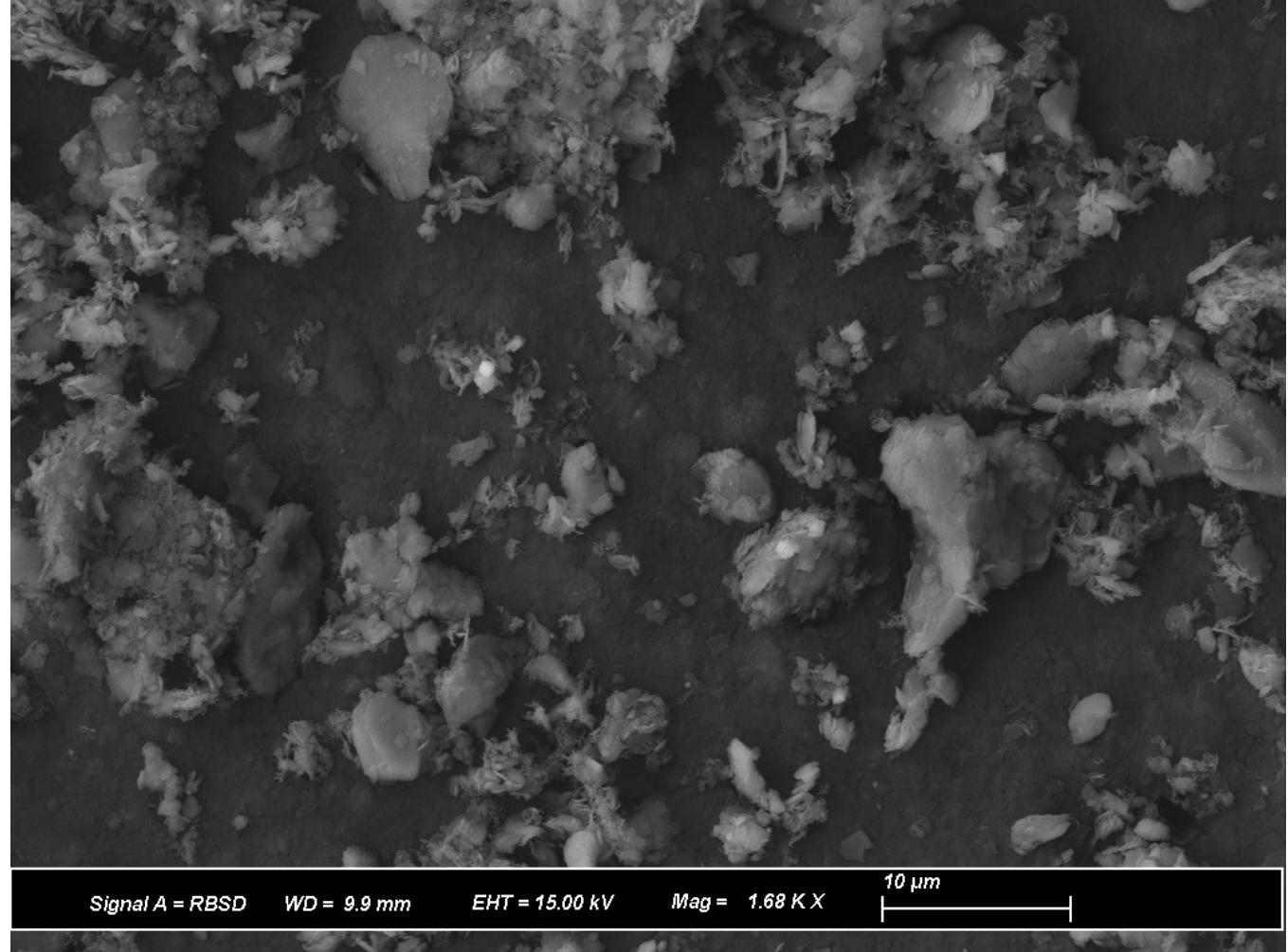
## Relative REE content in anthracite ash



# Characterization

## Particle morphology of anthracite ash

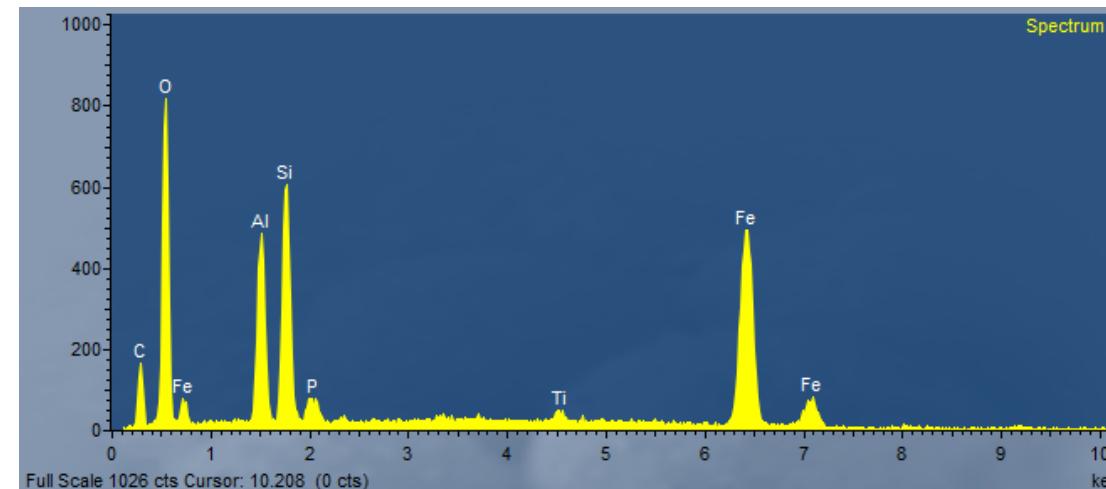
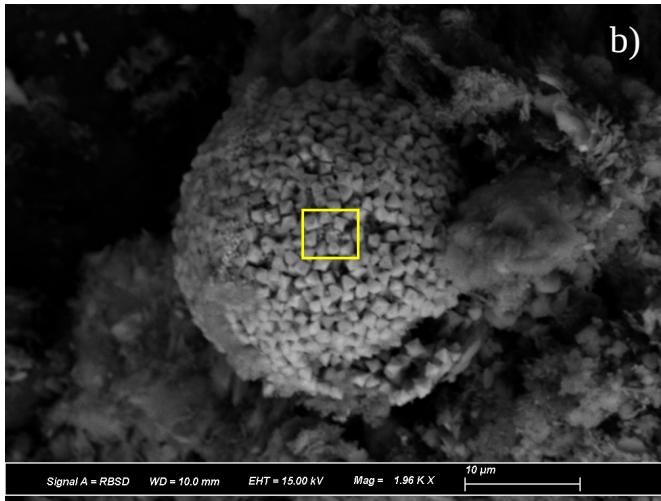
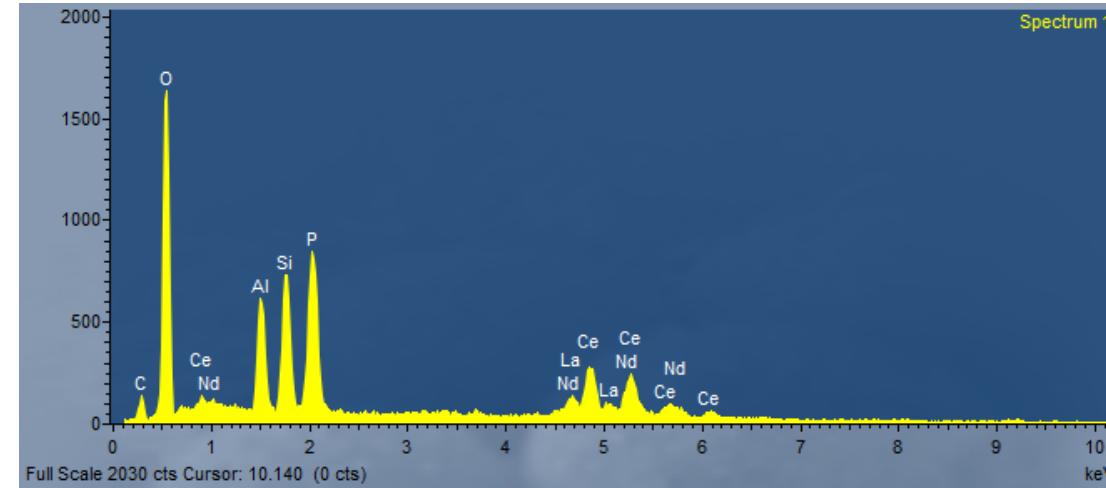
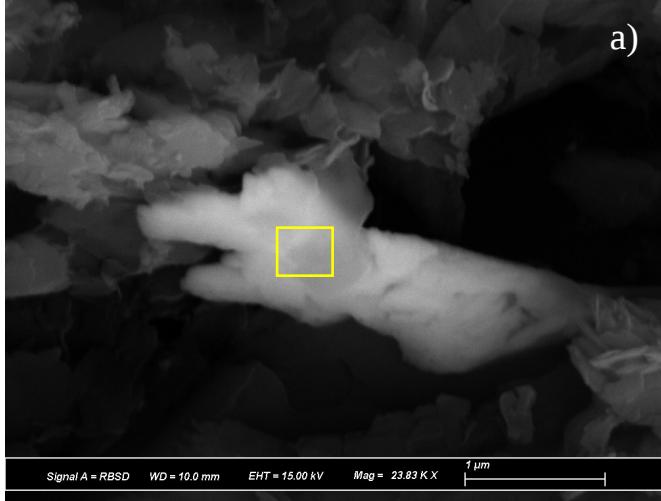
- Disperse
- Angular
- Size range: 1 to 10 um



*SEM microphotograph of anthracite ash*

# Characterization

## Particle morphology of anthracite ash



*SEM microphotographs and respective EDS spectra of a) REE particle; b) agglutination of minerals*

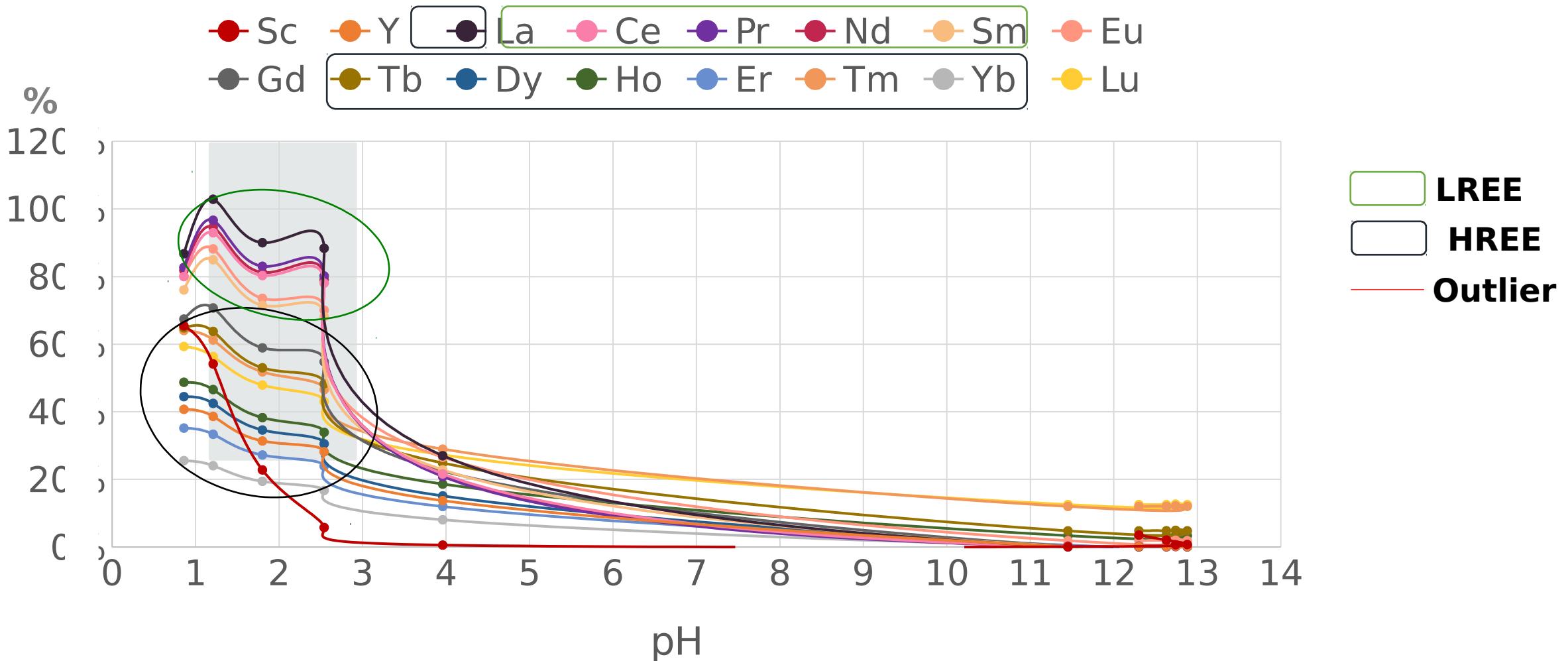
### Trace elements

- Carbon
- Oxygen
- Aluminum
- Silicone
- Phosphorus
- Titanium
- Iron

### REEs

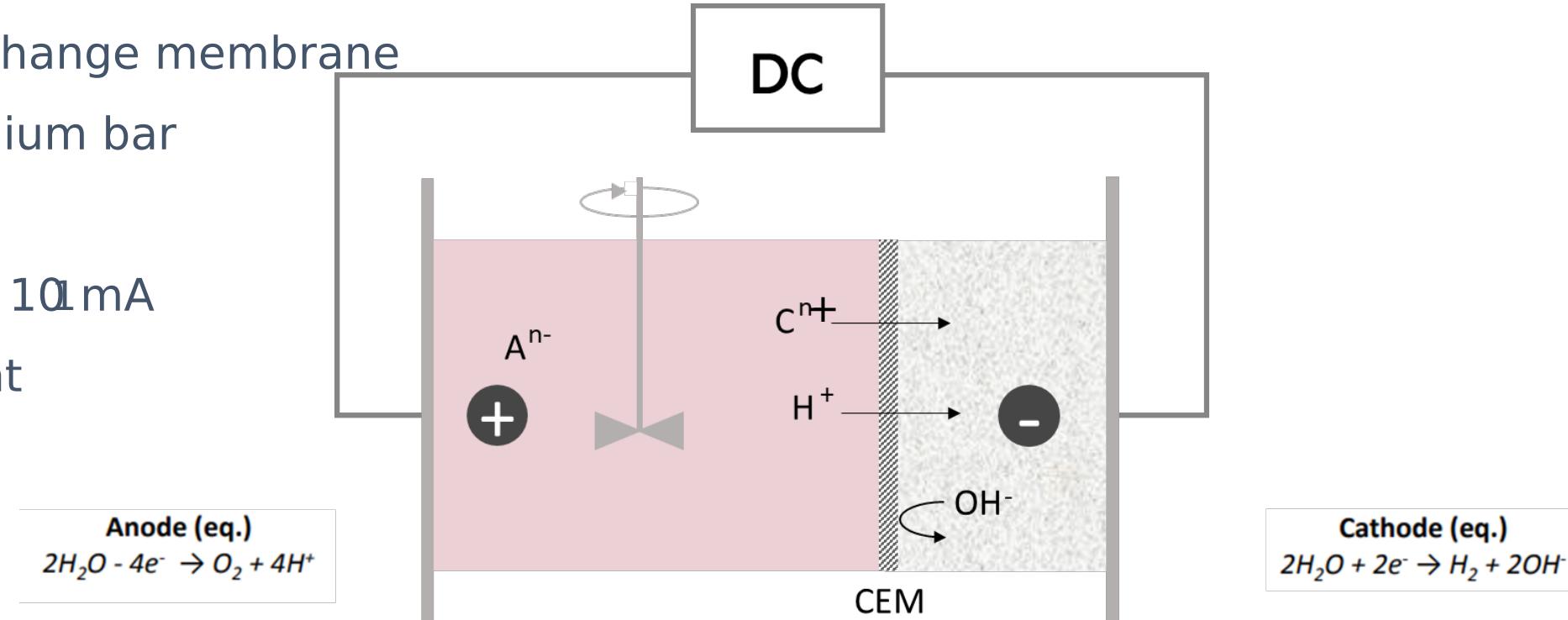
- Lanthanum
- Neodymium
- Cerium

# pH desorption from anthracite ash



# ED experiments

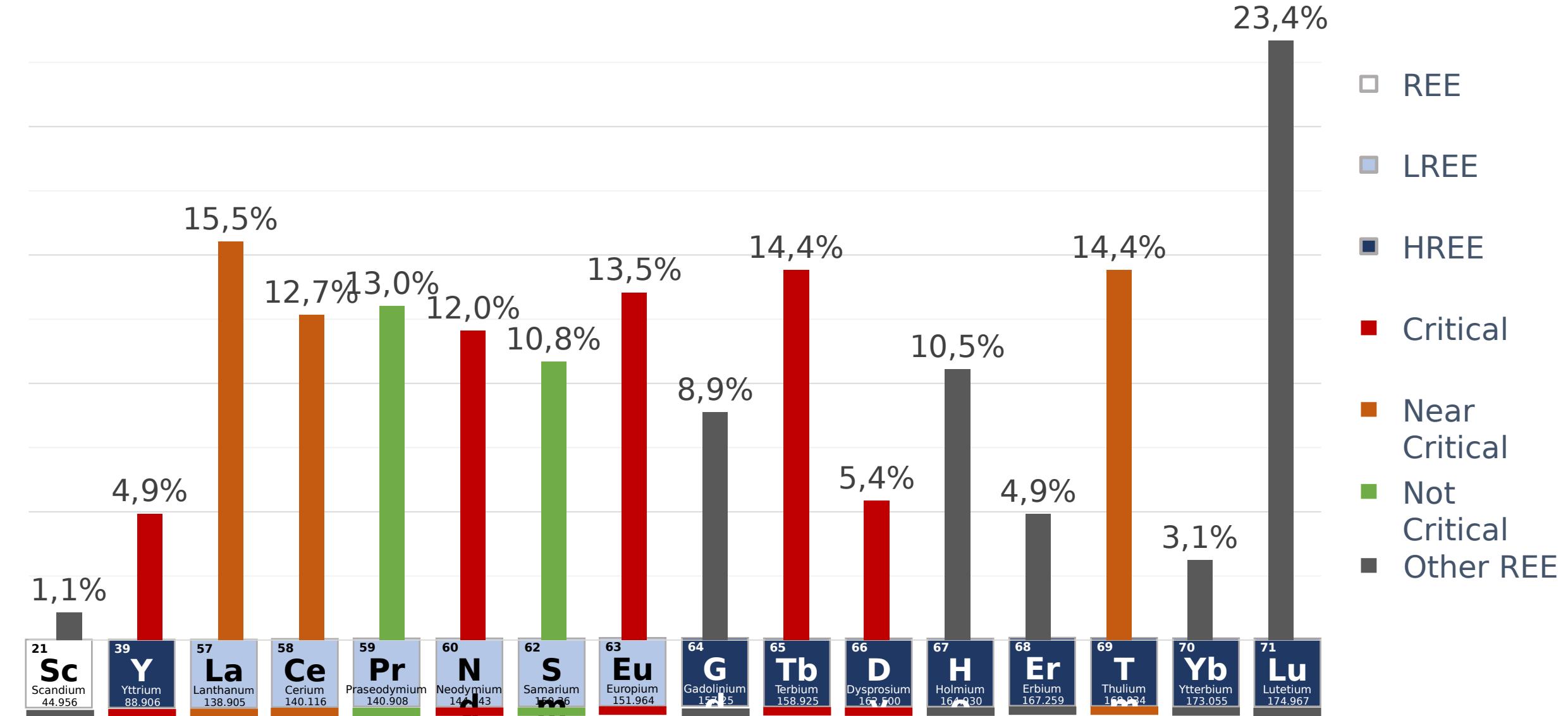
- 2C-ED cell
- L/S = 15
- CEM = cation exchange membrane
- MMO coated titanium bar
- Time: 3 days
- Current intensity: 10 mA
- pH: no adjustment



Ferreira et al. 2019, *Water Air & Soil Pollution*, 230(4): 78-88.

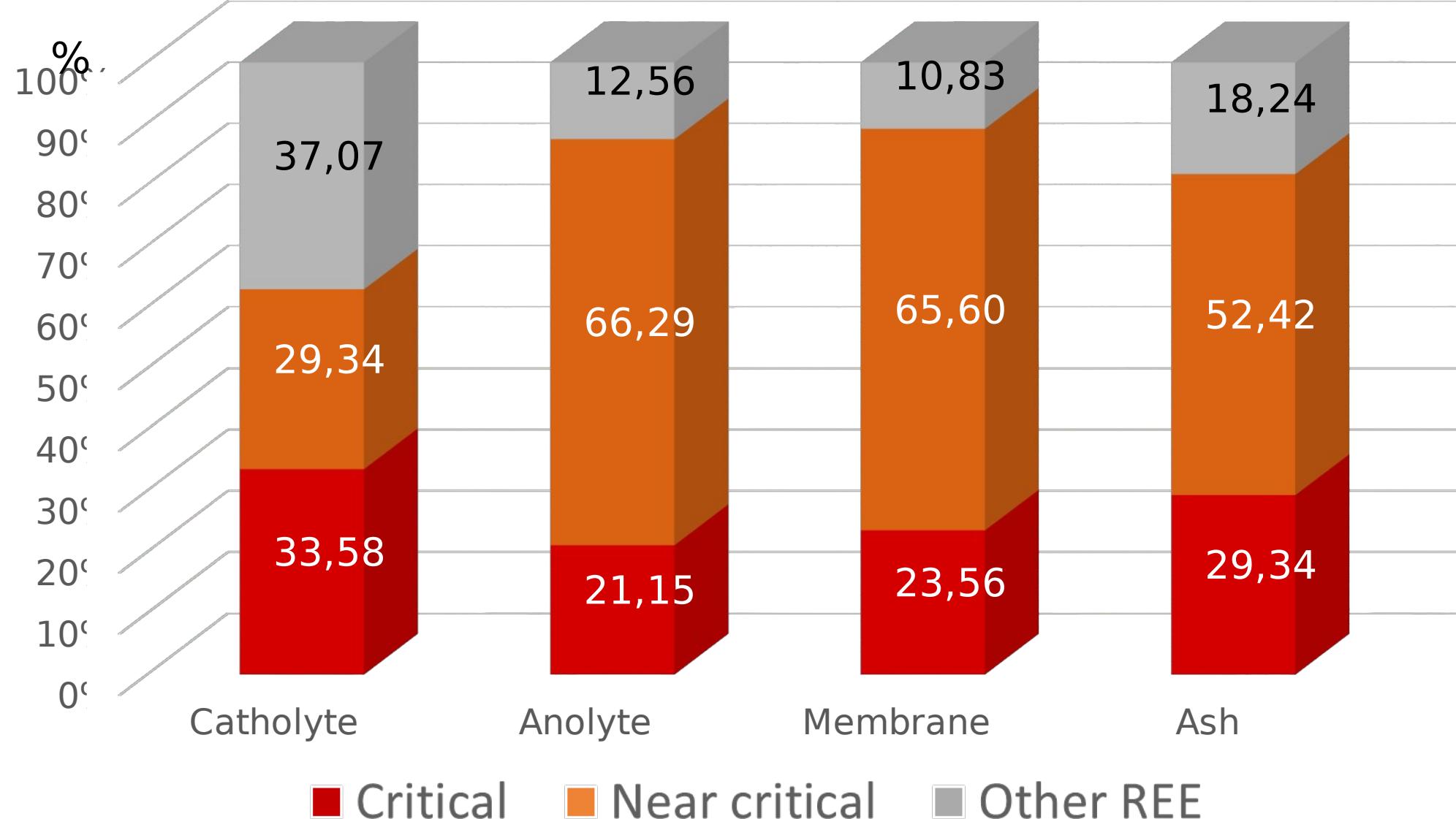
# Results

## Desorped REEs after ED



# Results

## REEs criticality analysis of relative content after ED



# Conclusions

ED process is a promising extraction technique for rare earth elements recover from coal ash

- REE desorption improved with the ED process
- LREE show higher desorption rates
- HREE show promising capabilities of passing through the CEM

Critical REEs	Relative % of REEs desorped by ED
Tb	14.4
Eu	13.5
Nd	12.0
Dy	5.4
Y	4.9

# References

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- Blaschak Coal Corporation, 2019. Representative analysis Lattimer mammoth vein. Accessed in June 2019 <http://www.blaschakcoal.com/wp-content/uploads/Lattimer-Mammoth-Vein-Rep-Analysis.pdf>
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# Acknowledgements

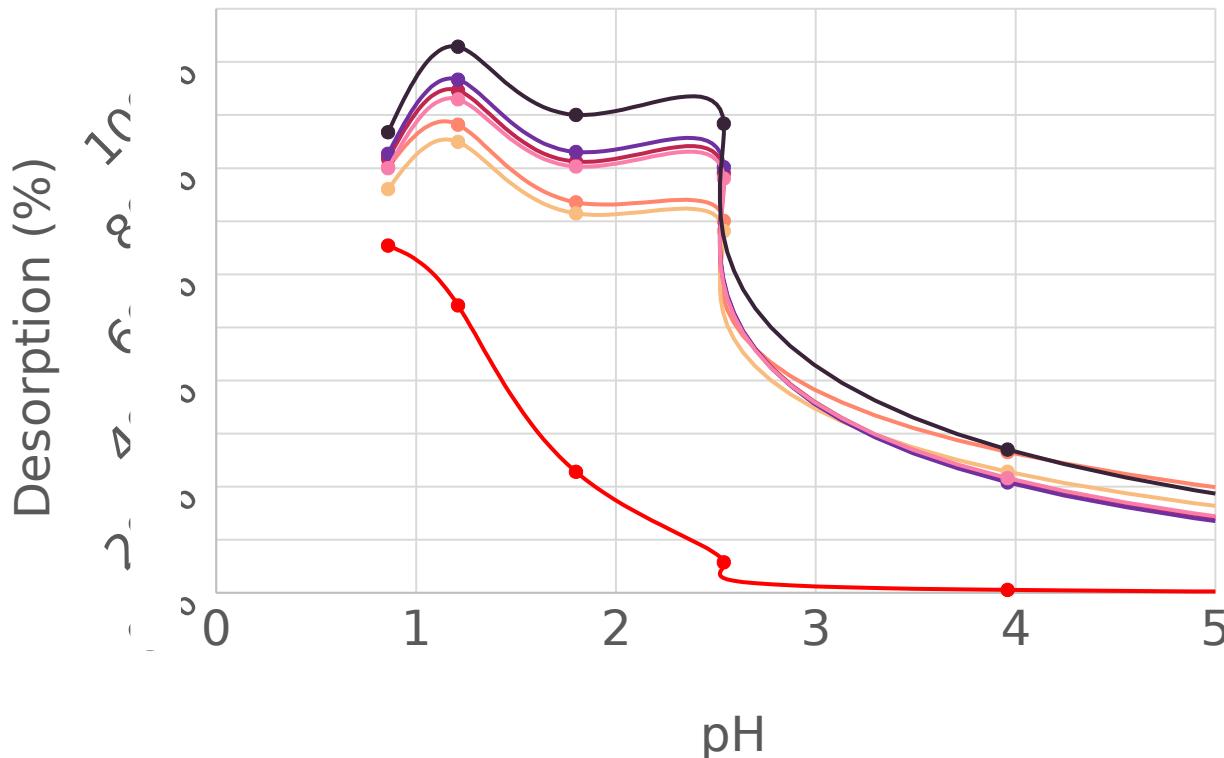


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# pH desorption

LREE

REE desorption at acidic pH



## LREE

- Stable complexes are the first to desorp
- Higher desorption rates compared to HREE

## Tendency

- Desorption starts from lower to higher atomic number (i.e. inversely related with ionic radius)

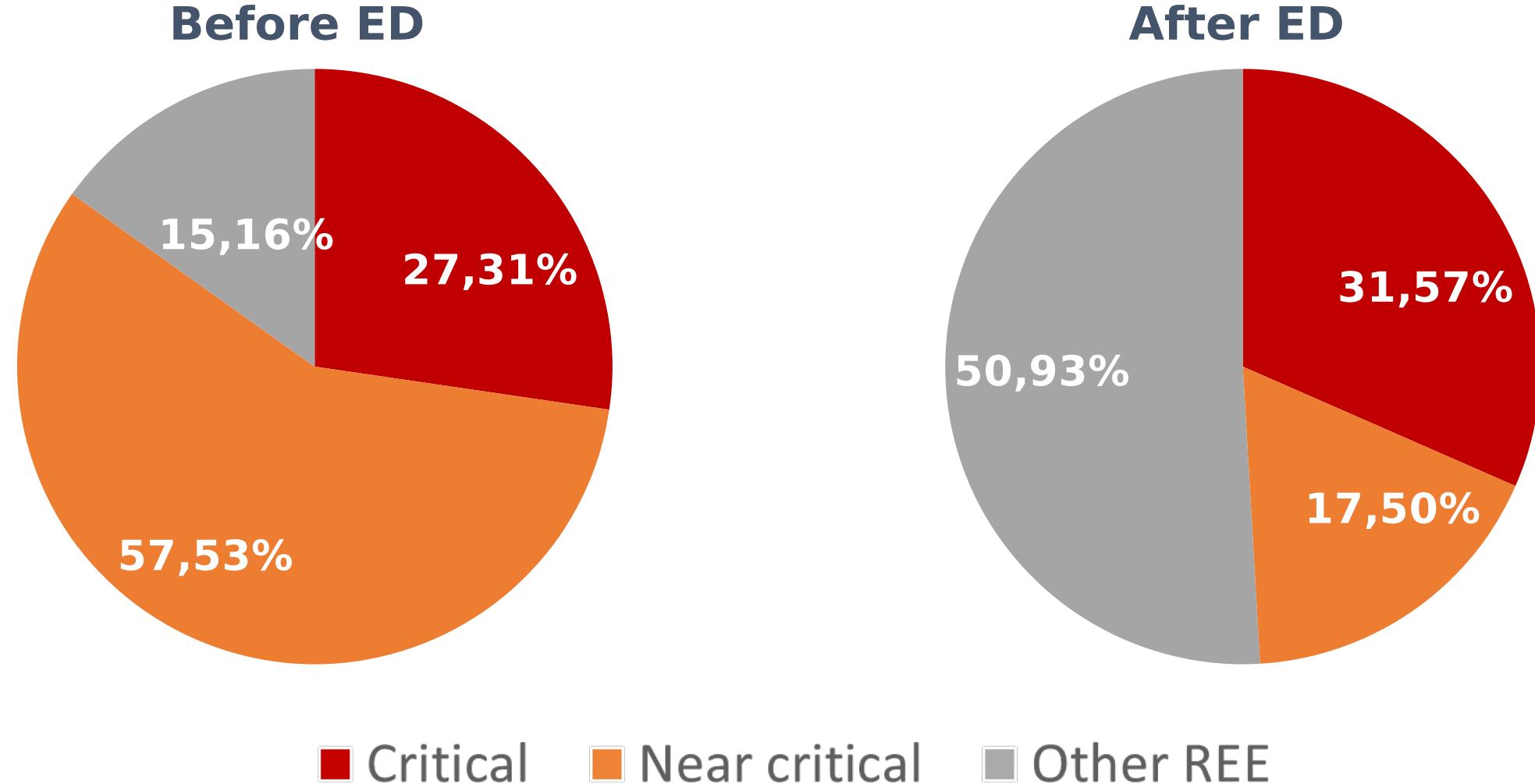
## Scandium

- Different electronic and magnetic properties

<b>21</b> <b>Sc</b> Scandium 44.956	<b>57</b> <b>La</b> Lanthanum 138.905	<b>58</b> <b>Ce</b> Cerium 140.116	<b>59</b> <b>Pr</b> Praseodymium 140.908	<b>60</b> <b>N</b> Neodymium 140.116	<b>62</b> <b>S</b> Samarium 150.966	<b>63</b> <b>Eu</b> Europium 151.964
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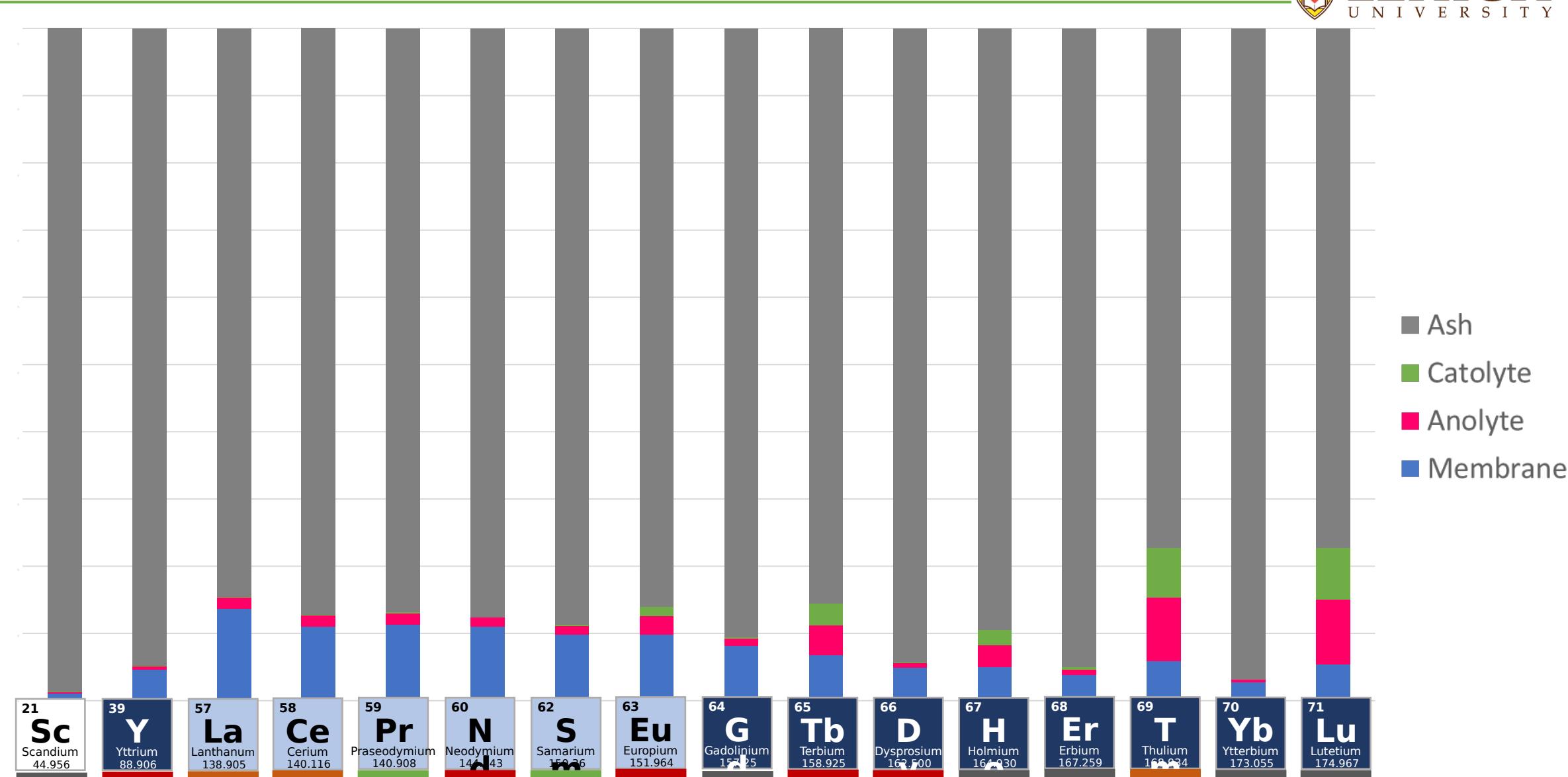
# Results

## Relative distribution of REEs in the ash



# Results

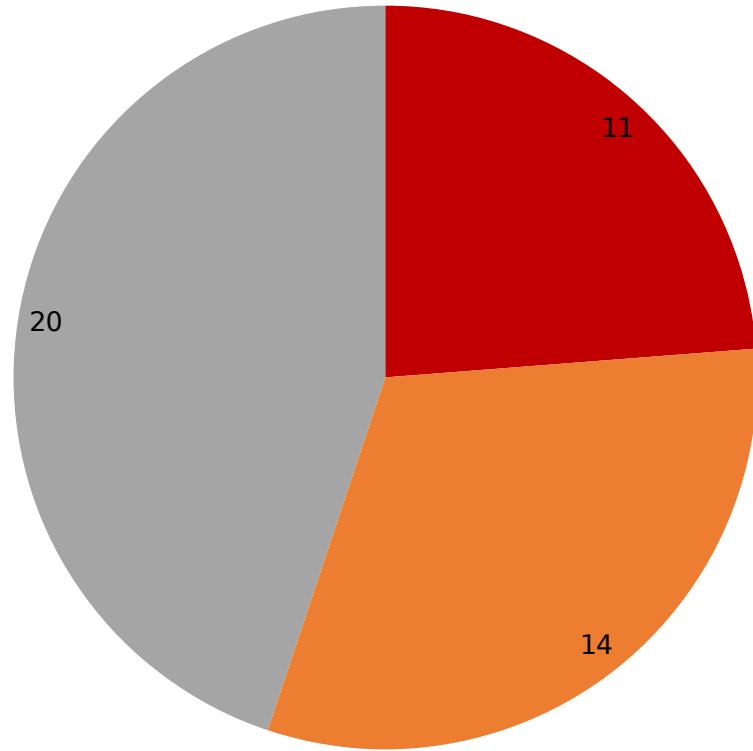
## REE distribution within the cell



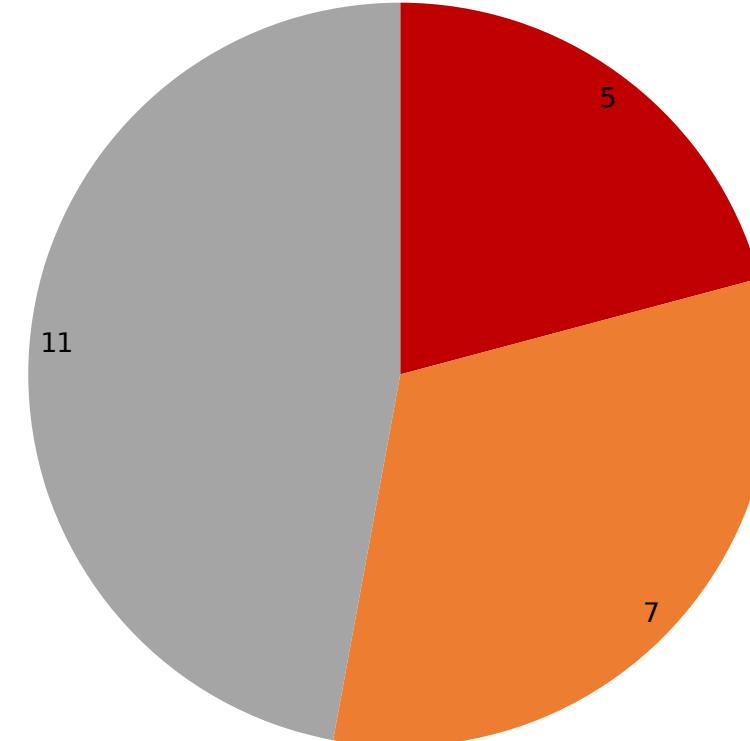
# Results

## Relative distribution of REEs in the liquid phase after ED

Anolyte



Catholyte



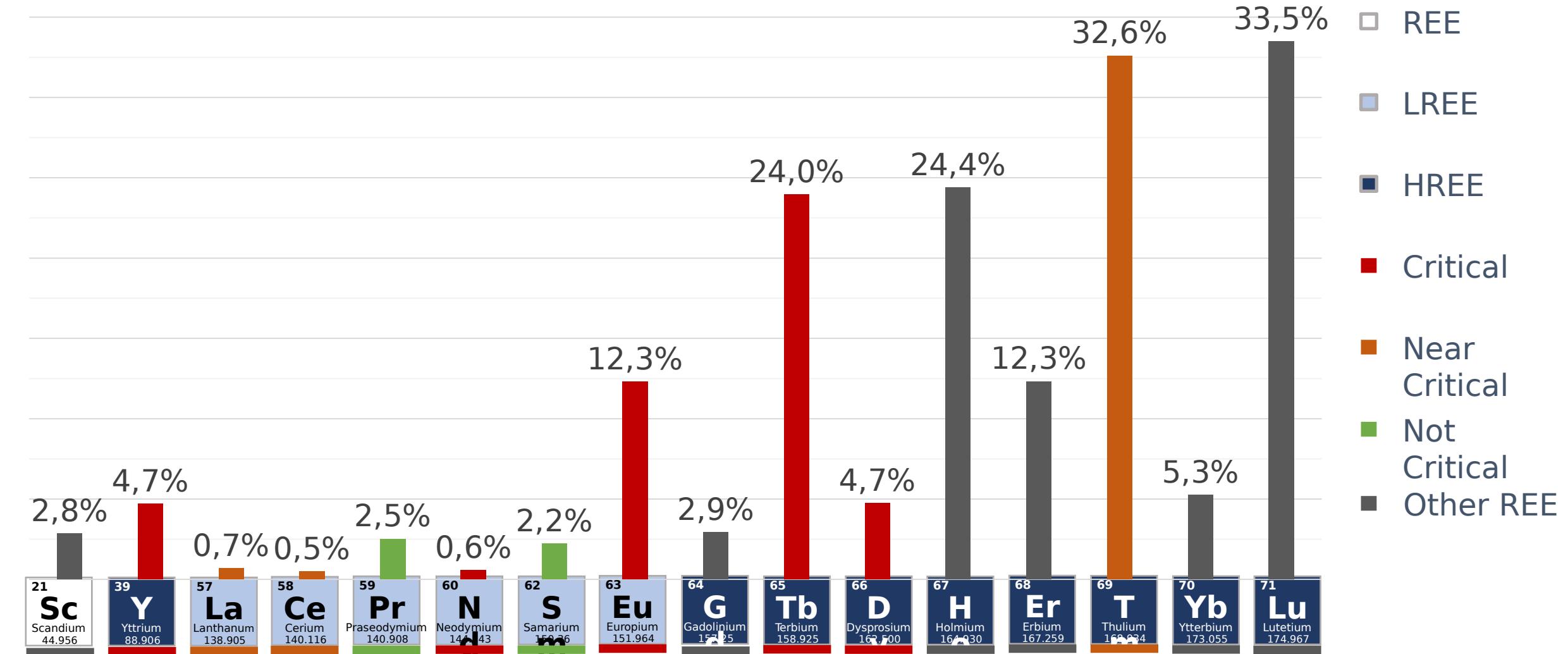
■ Critical

■ Near critical

■ Other REE

# Results

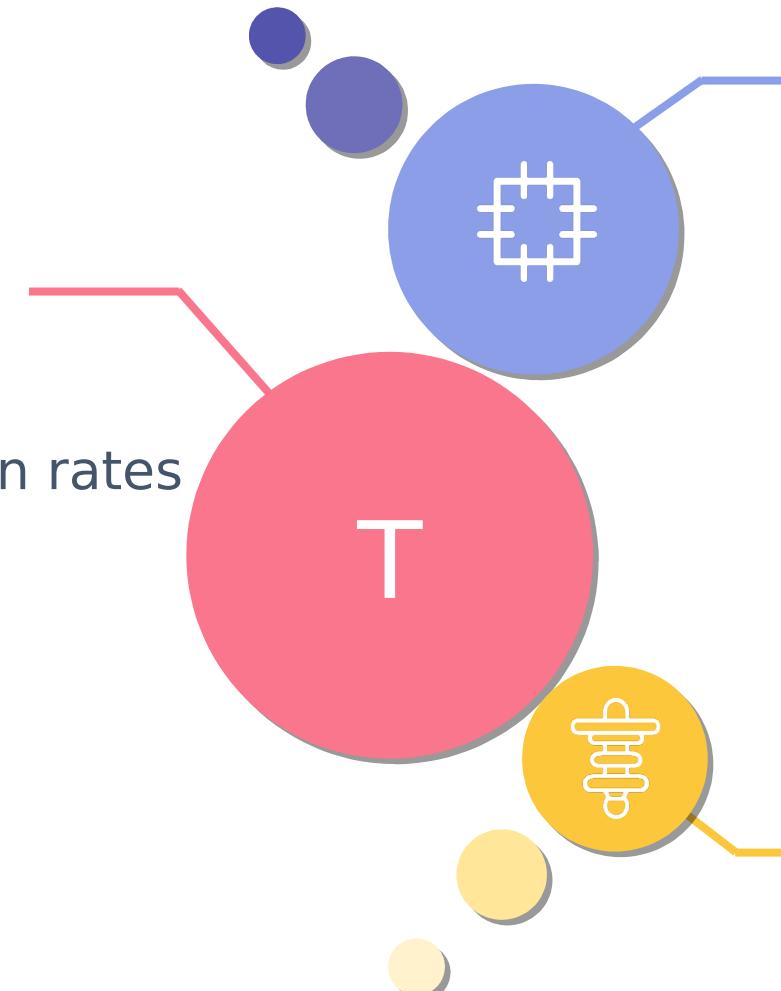
## REE in the catholyte after ED



# Future Work

## Experiment duration / days

- ✓ Higher desorption rates



## pH adjustment

- In the catholyte ( $\text{pH} \sim 2$ )
- ✓ Prevention of ion element precipitation
- ✓ Prevention of the formation of aggregated elements around the electrodes and the membrane
- ✓ Prevent membrane obstruction

## Increase current intensity

- ✓ Higher desorption rate
- ✓ Higher migration speed of the REE from the anolyte to the catholyte