



The University of Texas at Austin
Energy Institute

Enabling the Sustainable Energy Transition: Economic Recovery of Rare Earth Elements

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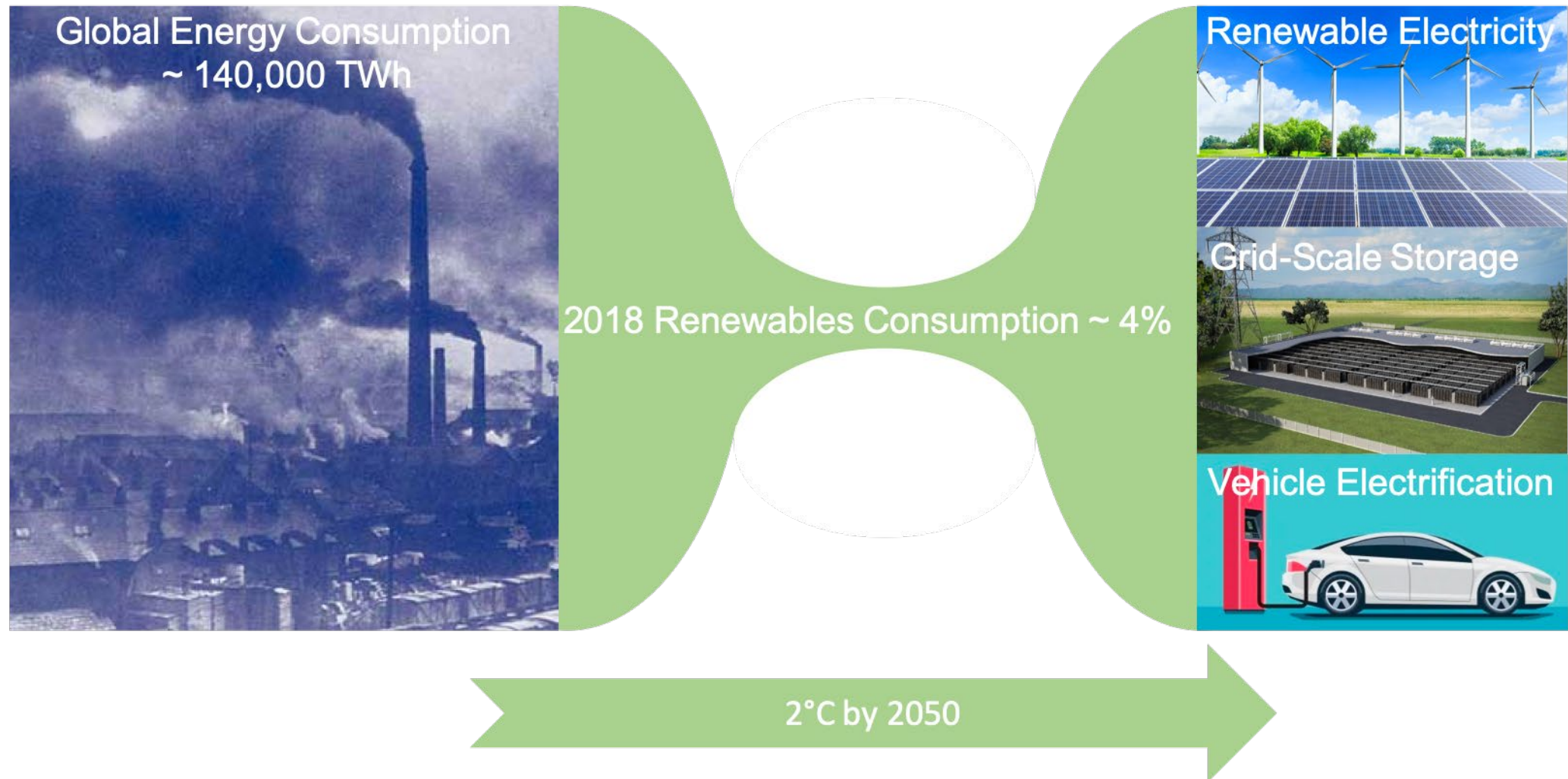
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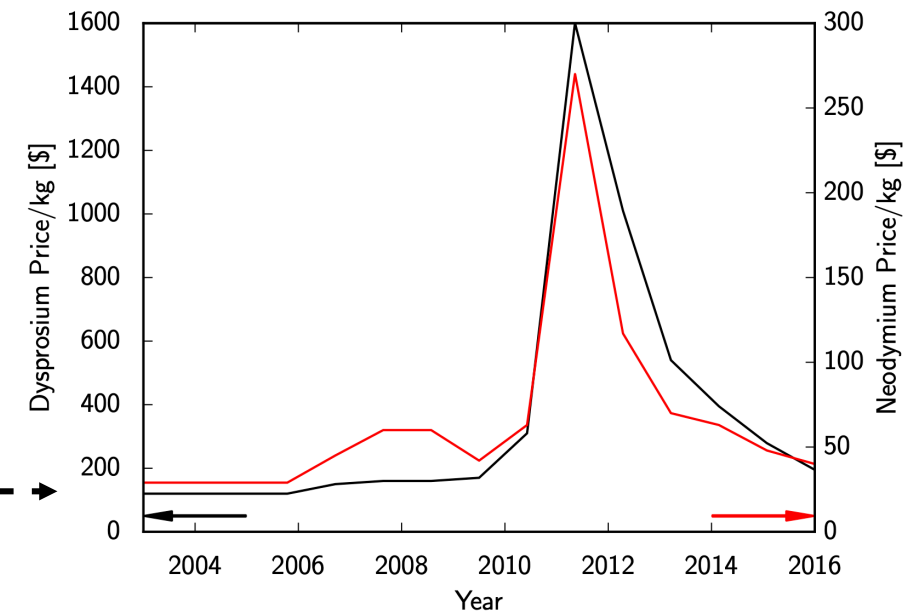
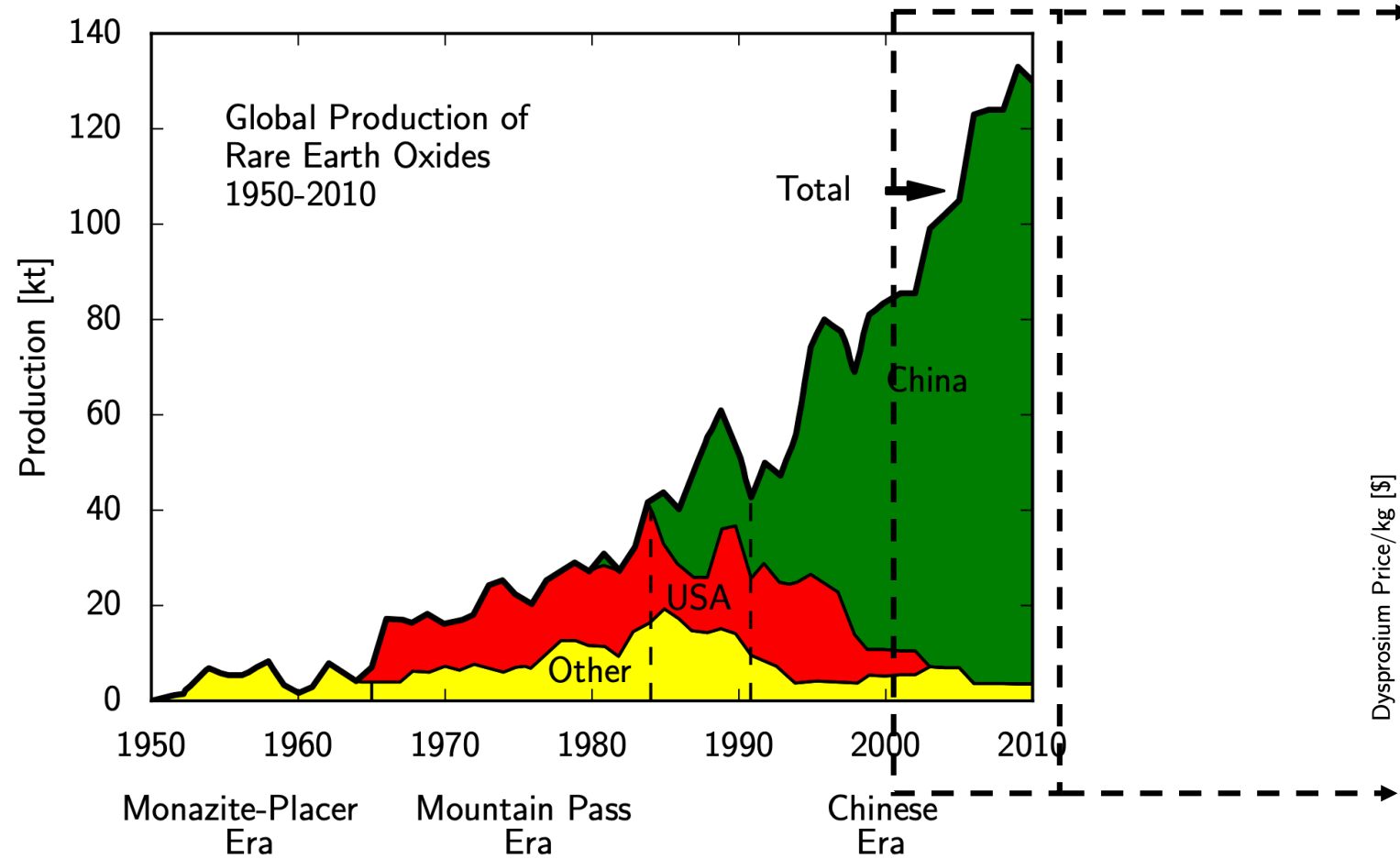
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March 1, 2022

Fueling a sustainable energy transition

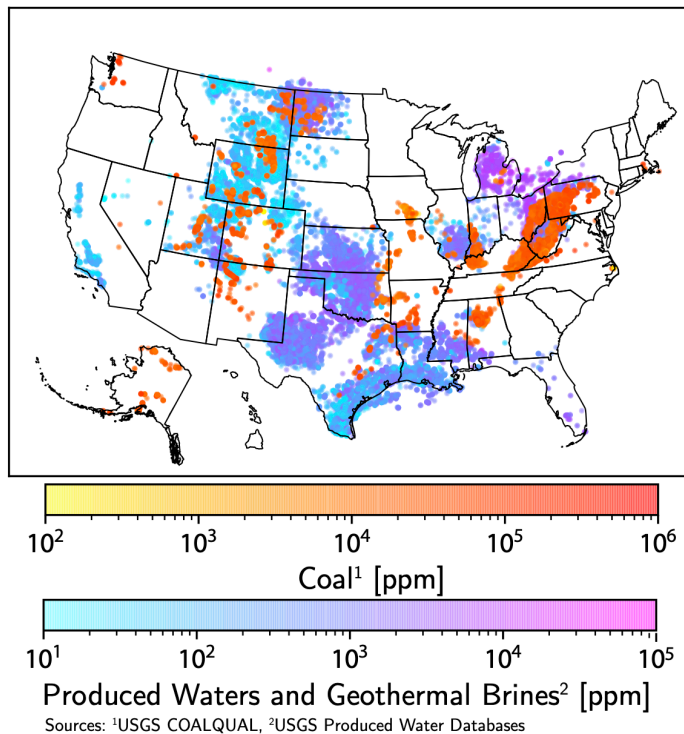


Global production of REEs

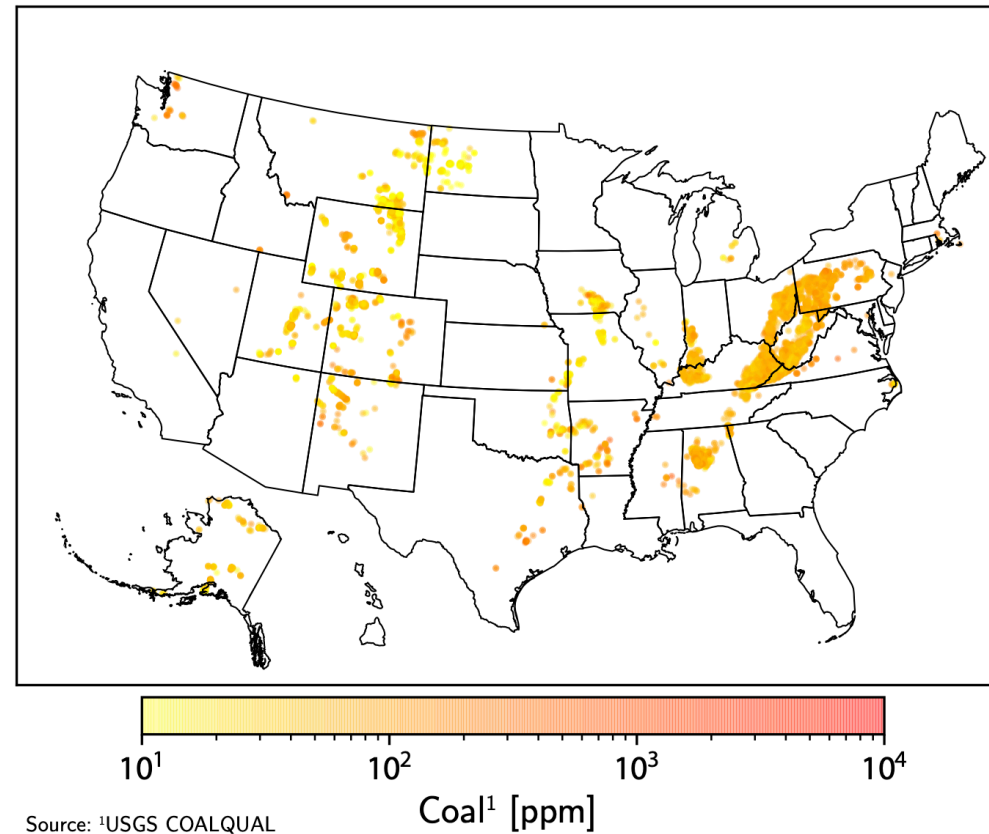


Unconventional resources for critical minerals

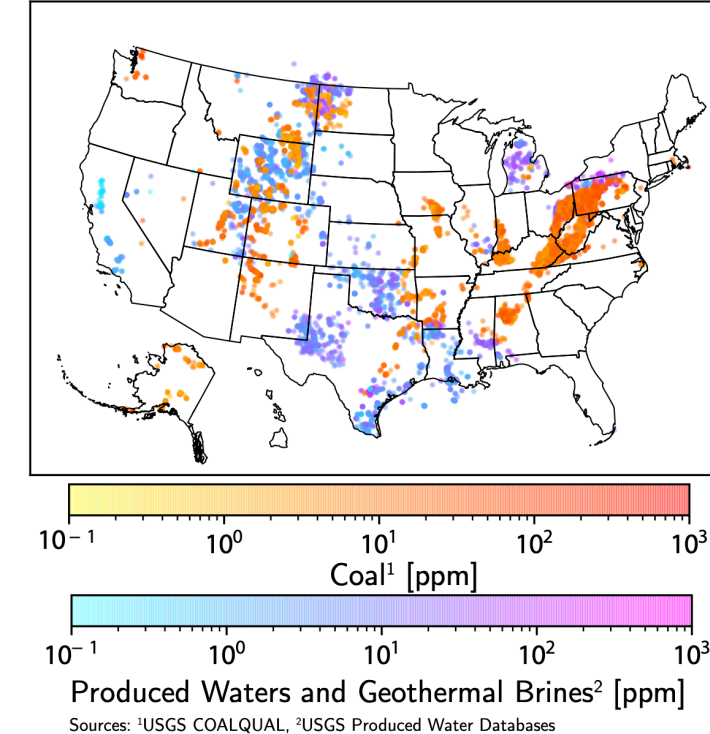
Total Concentration of CMs



Total Concentration of REEs

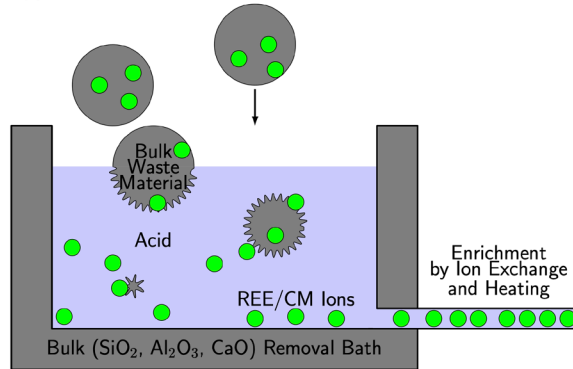


Total Concentration of Li

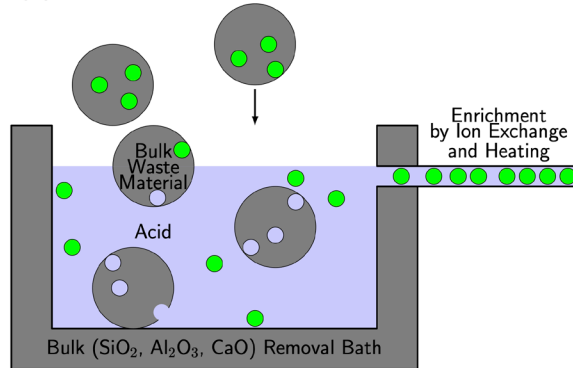


Our Technology: Enriched Plasma Separation

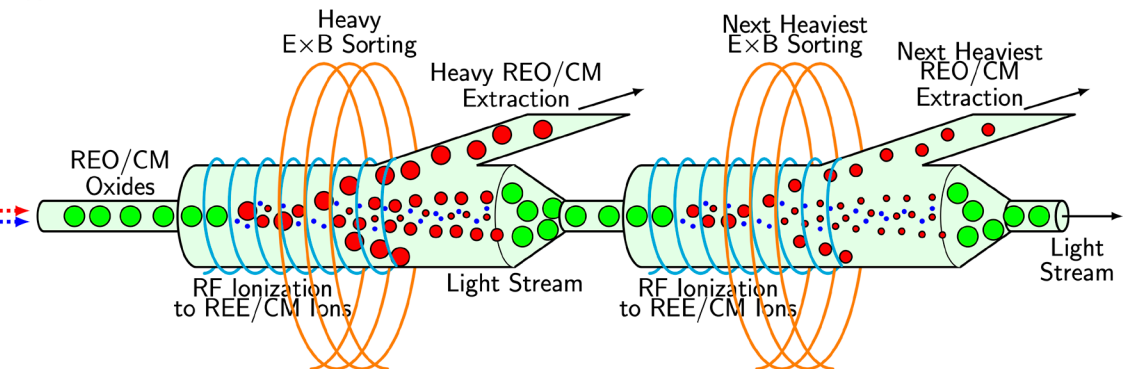
(a) Initial Acid Treatment
(i) Fly Ash



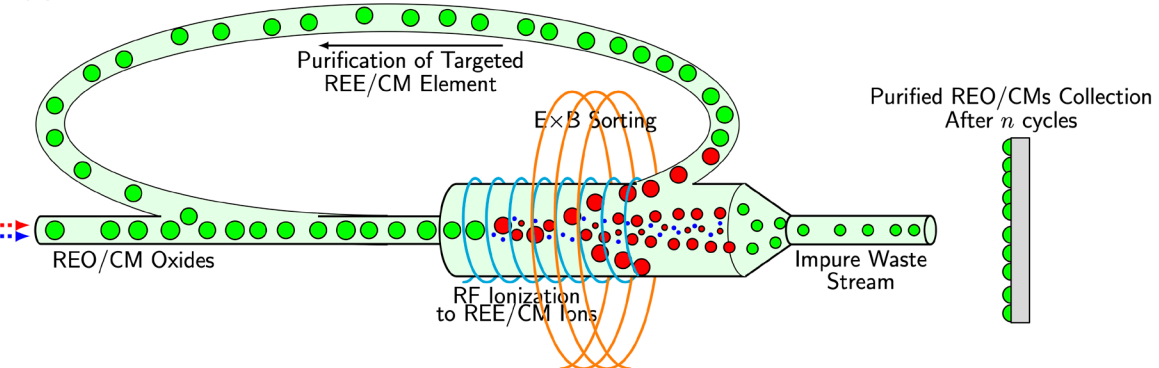
(ii) Coal, Interlayer Material, and AMD Sludge



(b) Plasma REE/CM Elemental Separation
(i) High Throughput Separation

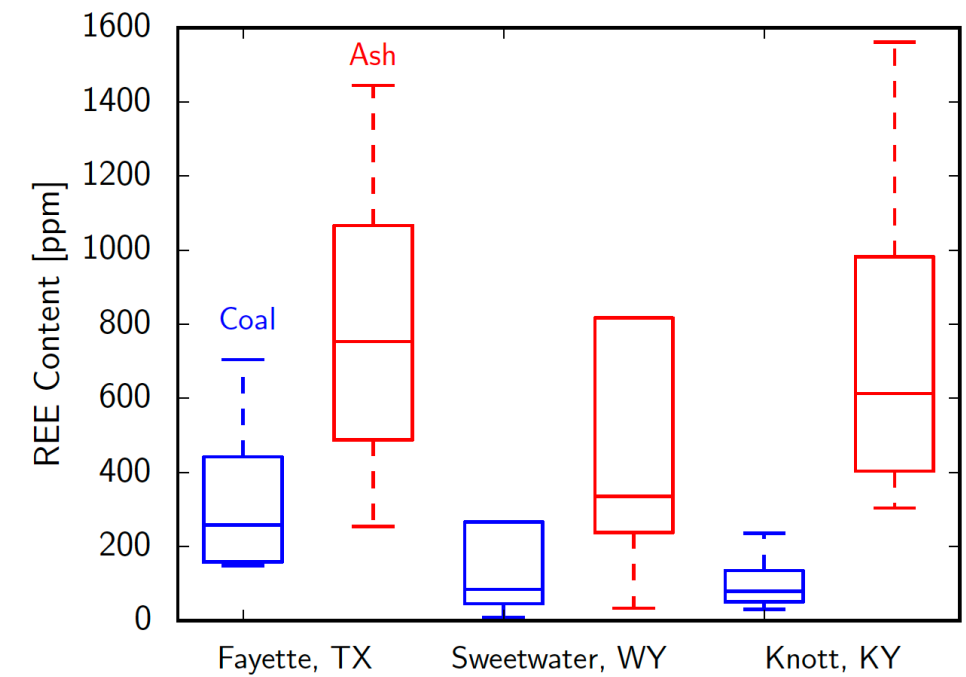
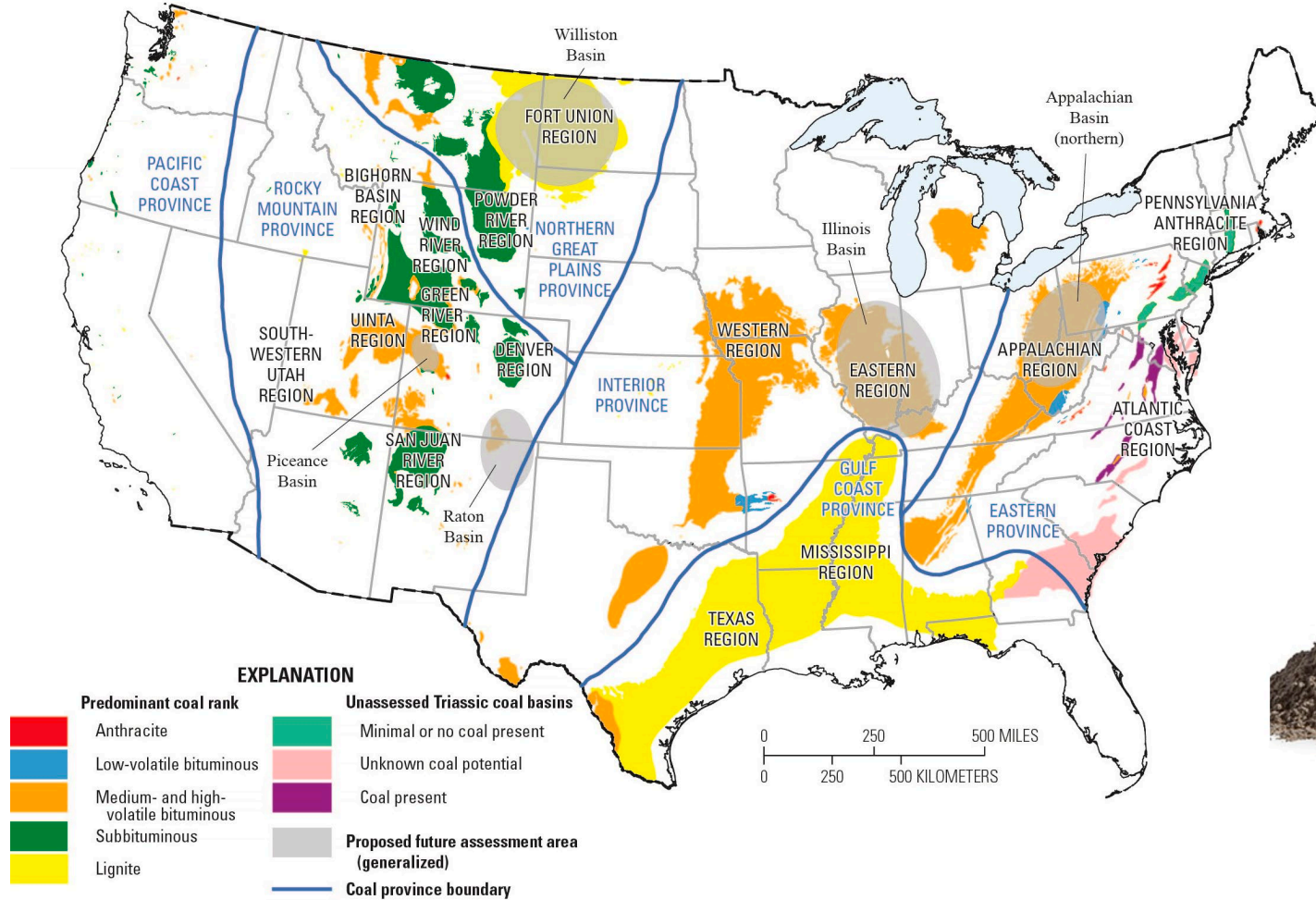


(ii) High Purity Separation

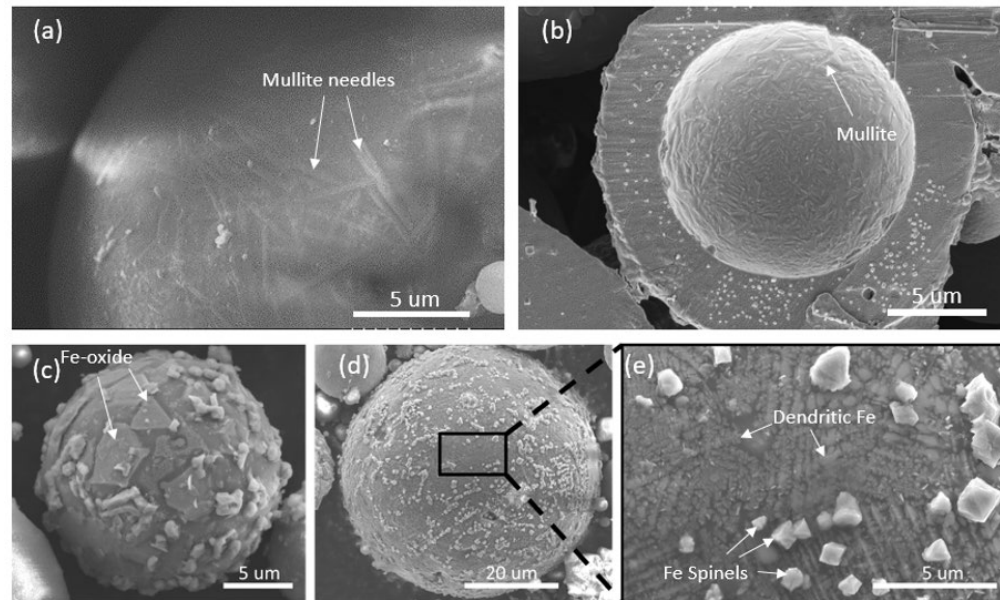


- Recovery up to 99% of available REEs, independent of feedstock composition
- Production of salable > 99% purity REE product
- Low secondary waste production

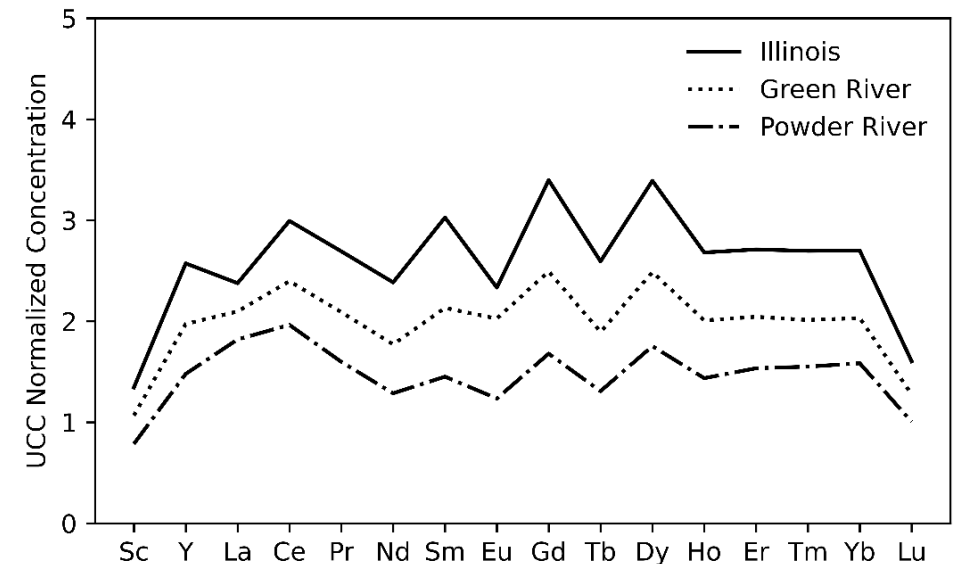
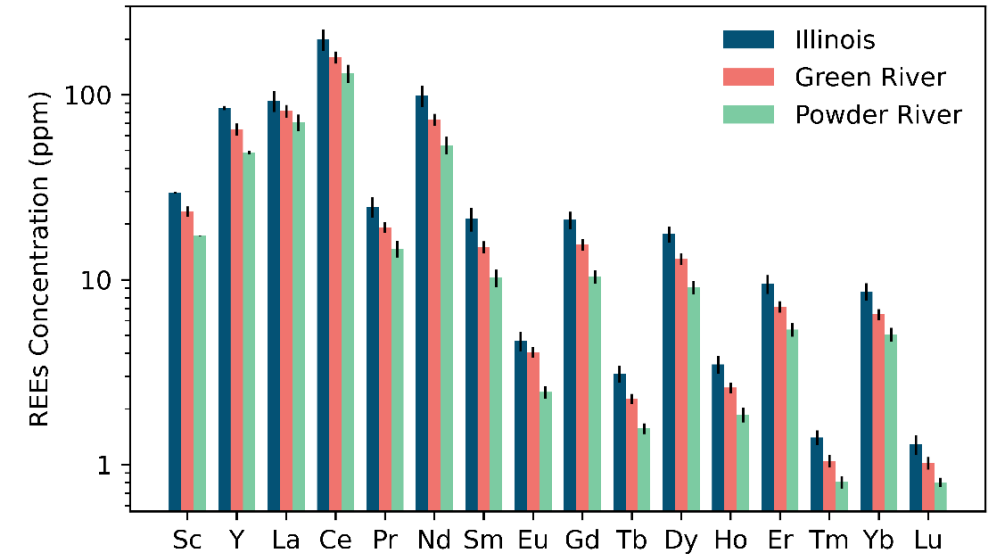
Resource characterization



Resource characterization

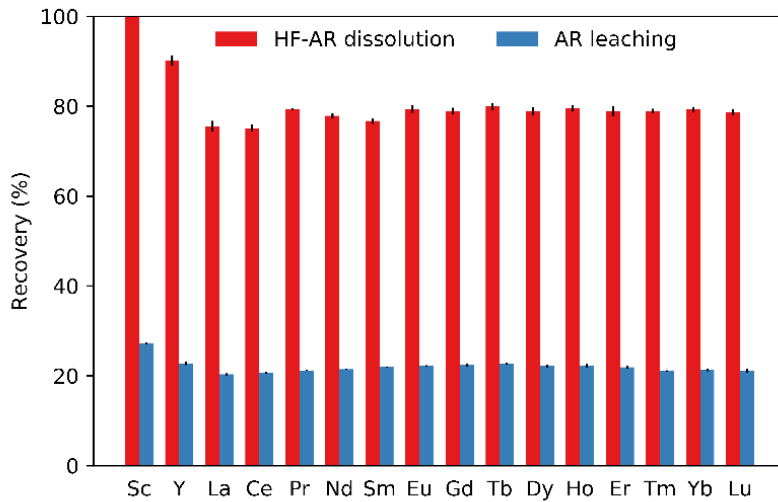


Basin	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	NaO	SiO ₂	TiO ₂
Illinois	20.6%	2.9%	22.1%	2.5%	1.0%	0.6%	49.4%	0.9%
Green River	17.1%	28.2%	5.8%	0.4%	6.7%	1.8%	38.0%	1.2%
Powder River	17.5%	6.0%	4.3%	1.2%	2.4%	1.6%	65.6%	0.9%

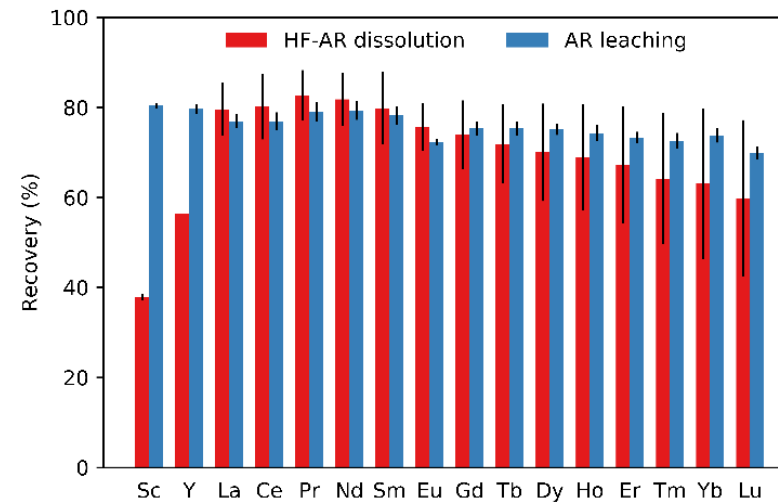


Reagents-based recovery of REEs

Illinois



Green River

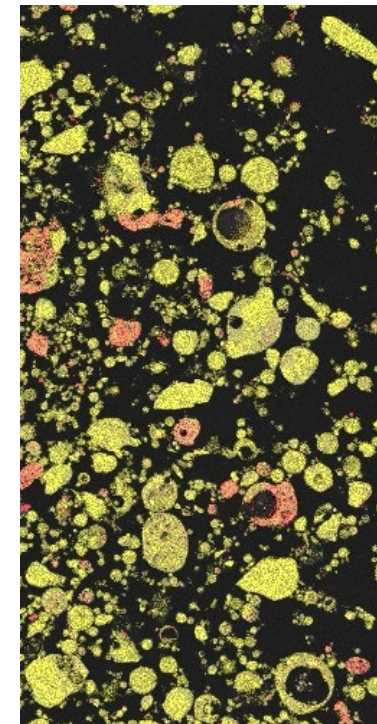


Initial



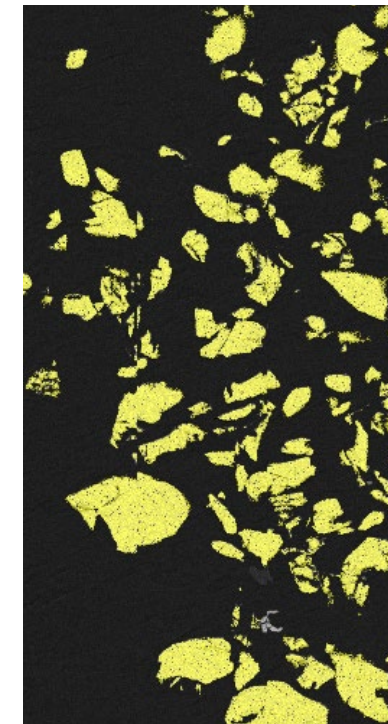
Si Al Ca

AR residue



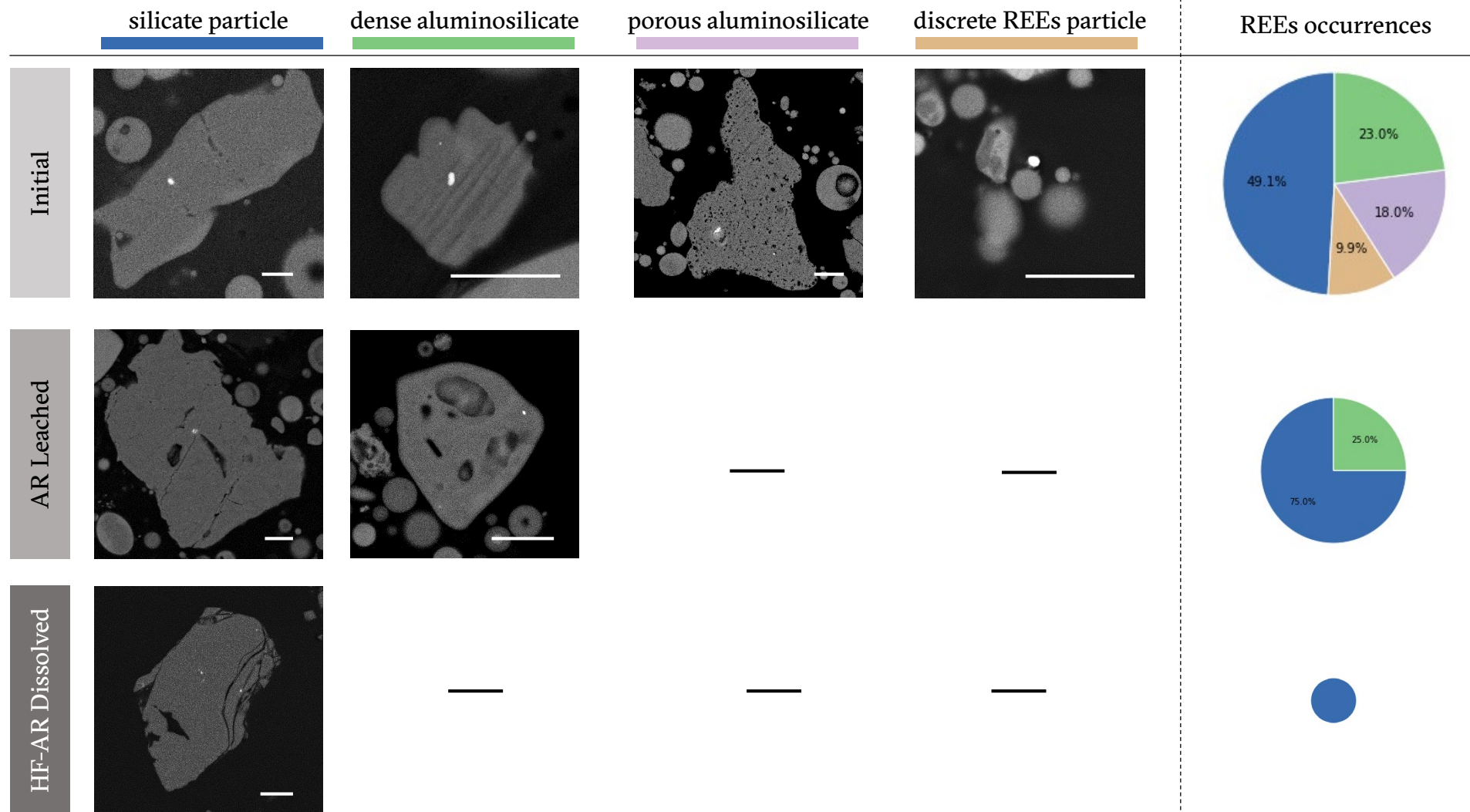
Si Al

HF-AR residue

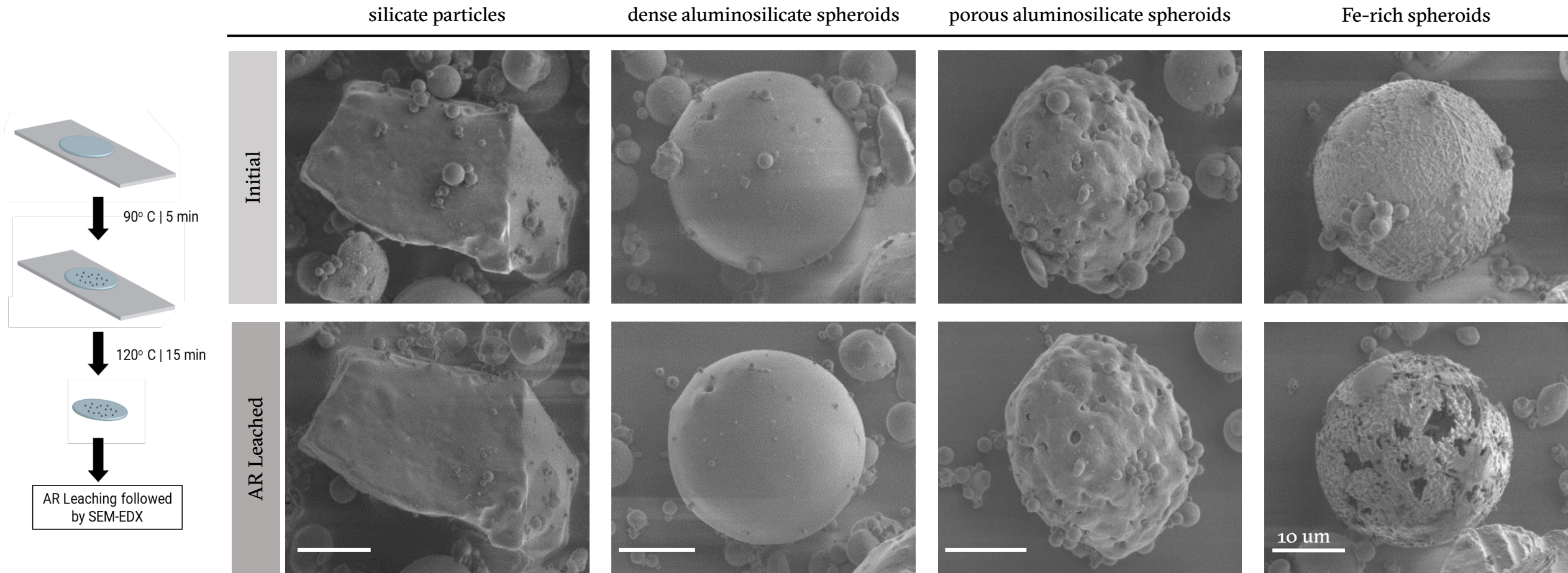


Si

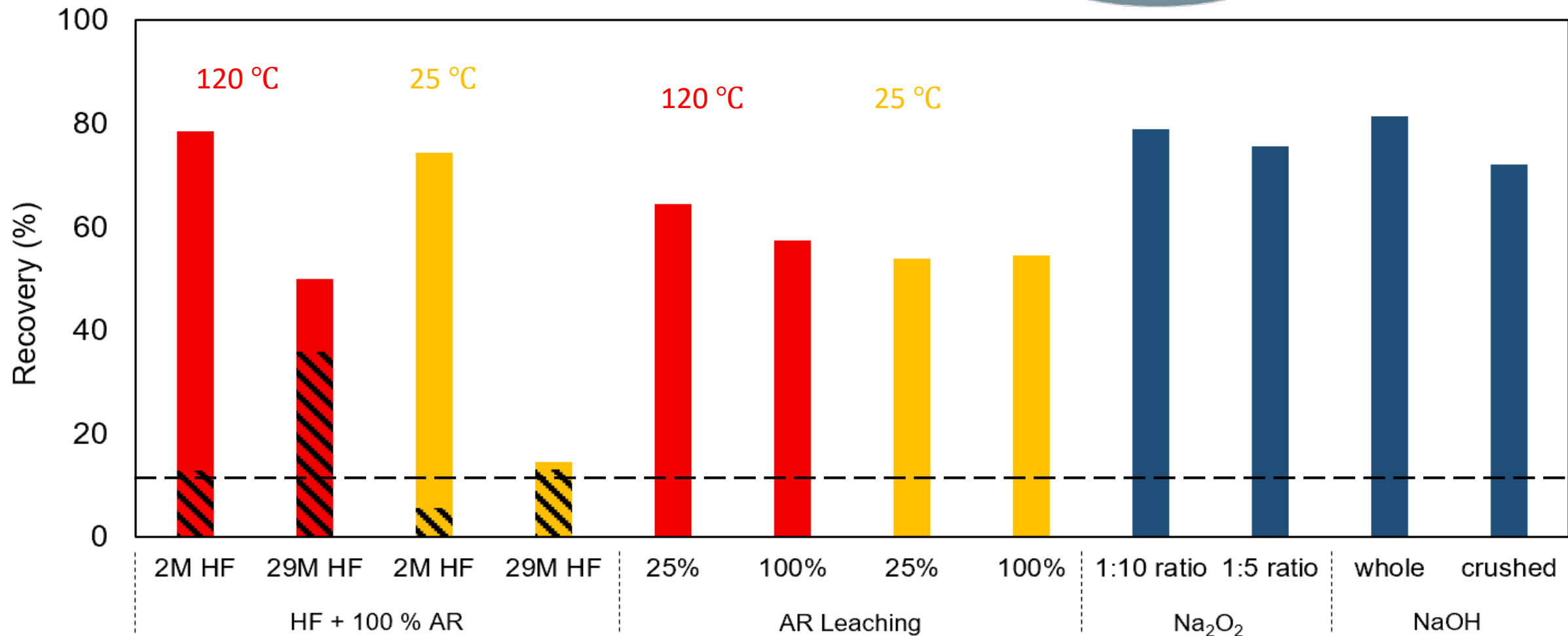
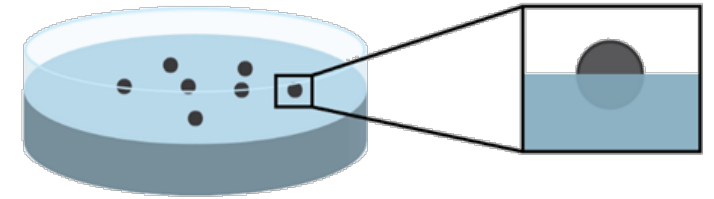
Micro/nano intraparticle porosity



Mineralogic heterogeneity on leaching

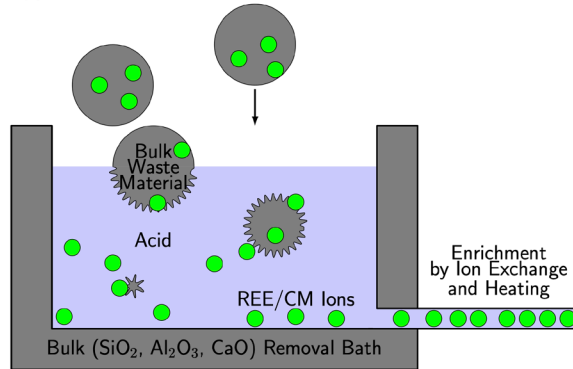


Improved, environmentally-benign REEs recovery

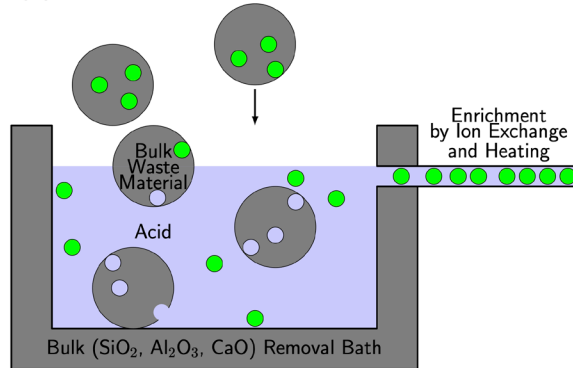


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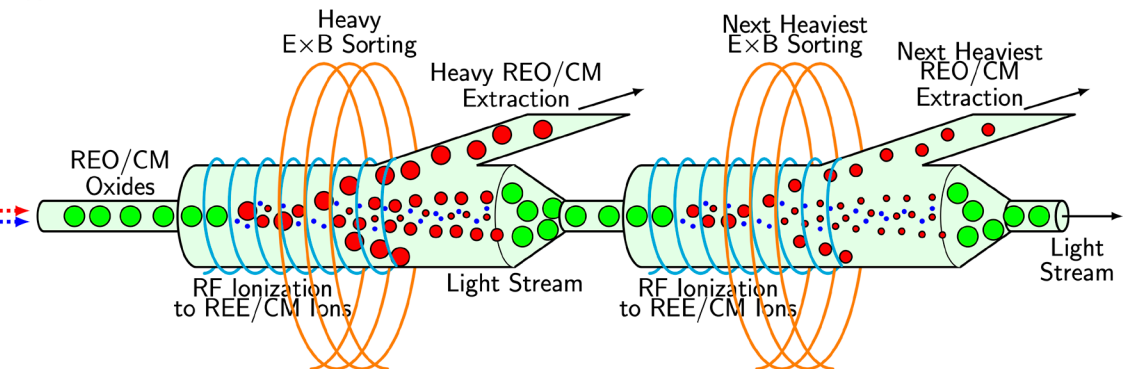
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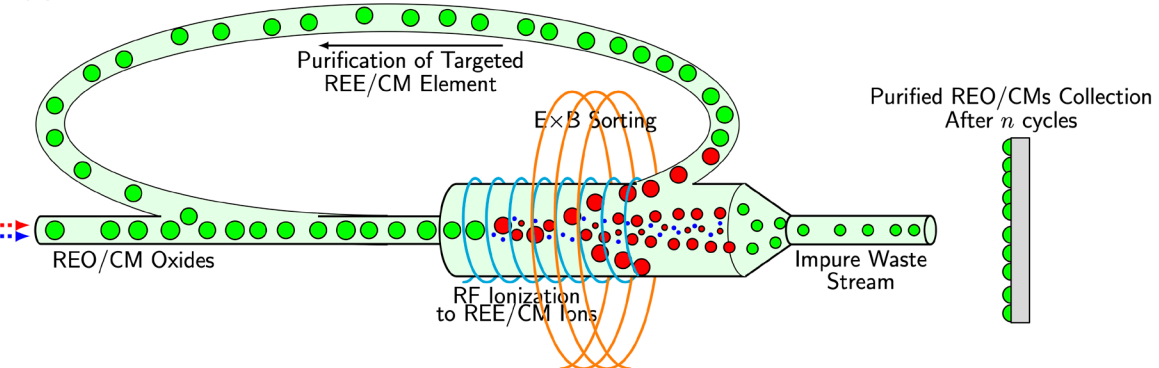
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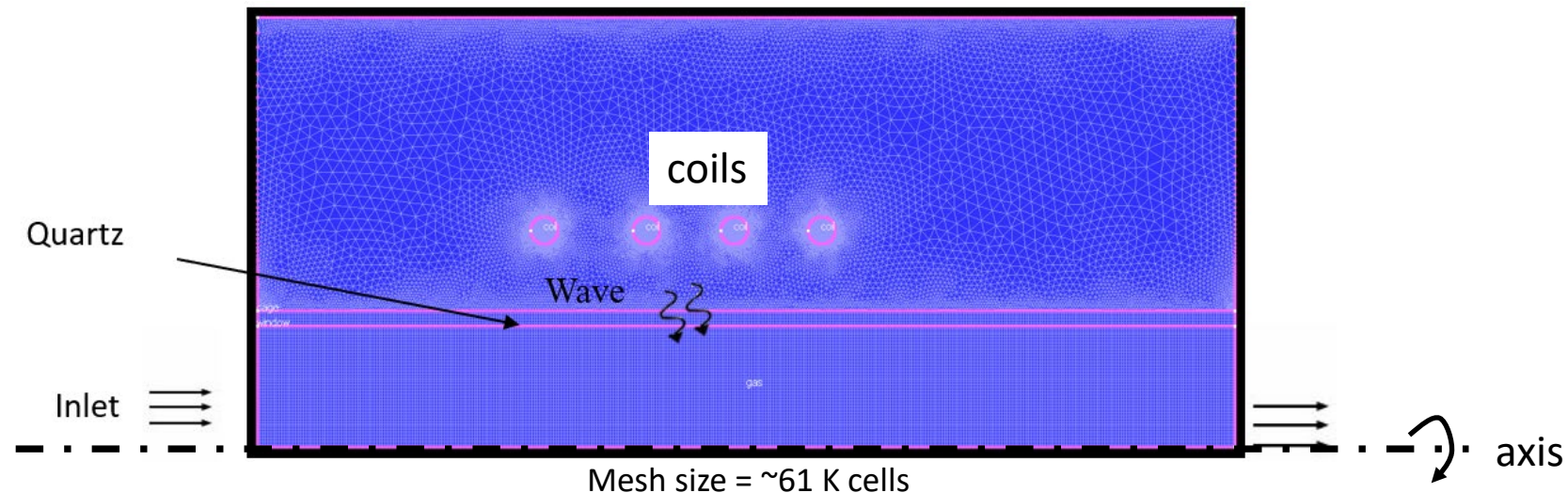
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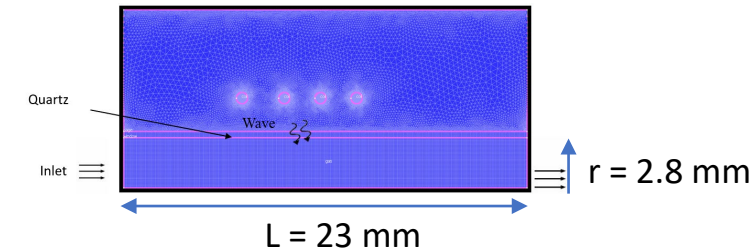
REE ionization (ICP inductively coupled plasma)

- ICP provide an electrodeless approach to plasma generation and gas ionization (including the RRE species)
- Key questions are:
 1. Optimal geometric requirements and operating conditions for stable ICP generation
 2. Ionization fraction of RRE species (process yield) transported into ICP



REE ionization studies based on plasma modeling

- We have performed extensive model-based exploration of the plasma parameter space (pressure, power, flow rates, discharge dimensions, etc.)
- Results indicate REE ionization fraction is strongly dependent on process pressure and power density into plasma
 - Higher pressures support higher ionization fraction
 - Smaller discharge dimensions support higher power density
 - Hence, we have chosen ~mm dia. ICP discharge as baseline geometry for studies



	Parameters		
Feed stream (with mole fraction)	Ar + Ce (10^{-5} mole fraction)		
Inflow Temperature	300 K		
Feed gas mass flow rate	$8.1 \times 10^{-8} \text{ kg/s}$ (50 sccm)		
Pressure	0.1 torr	1 torr	100 torr
EM Power	1 W		

Plasma chemistry for argon carrier gas with cerium (Ce) as REE surrogate

#	RXN	RXN Type	RXN Energy (eV)	Ref.
1	$\text{Ar} + \text{E} \rightarrow \text{Ar}^* + \text{E}$	Excitation	11.56	BOLSIG
2	$\text{Ar} + \text{E} \rightarrow \text{Ar}^+ + 2\text{E}$	Ionization	15.76	BOLSIG
3	$\text{Ar}^* + \text{E} \rightarrow \text{Ar}^+ + 2\text{E}$	Step-wise Ionization	4.2	BOLSIG
4	$\text{Ar}^+ + \text{E} \rightarrow \text{Ar}^*$	Radiative Recombination	0.0	[1]
5	$2\text{Ar}^* \rightarrow \text{E} + \text{Ar} + \text{Ar}^+$		-7.56	[1]
6	$\text{Ar}^* + \text{E} \rightarrow \text{Ar} + \text{E}$	De-excitation	-11.56	BOLSIG
7	$\text{Ar}^* + \text{Ar} \rightarrow 2\text{Ar}$	De-excitation	-11.56	BOLSIG
8	$\text{Ar}^* \rightarrow \text{Ar}$	Radiative Decay	0.0	[1]
9	$2\text{E} + \text{Ar}^+ \rightarrow \text{E} + \text{Ar}^*$	3-Bdy Recombination	-4.2	[1]
10	$\text{Ar}^* + 2\text{Ar} \rightarrow \text{Ar}_2^* + \text{Ar}$		-0.6	[1]
11	$\text{Ar}^+ + 2\text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar}$		-1.3	[1]
12	$\text{E} + \text{Ar}_2^* \rightarrow 2\text{E} + \text{Ar}_2^+$		3.5	[1]
13	$\text{E} + \text{Ar}_2^* \rightarrow 2\text{Ar} + \text{E}$		-10.96	[1]
14	$\text{Ar}_2^* \rightarrow 2\text{Ar}$	Radiative Decay	0.0	[1]
15	$2\text{Ar}_2^* \rightarrow \text{Ar}_2^+ + 2\text{Ar} + \text{E}$		-7.46	[1]
16	$\text{E} + \text{Ar}_2^+ \rightarrow \text{Ar}^* + \text{Ar}$		0.0	[1]
17	$\text{E} + \text{CE} \rightarrow 2\text{E} + \text{CE}^+$			[2]

Reaction 17: REE surrogate ionization based on theory

$$r(T) = kn_A n_B = Z\rho \exp\left(\frac{-E_a}{RT}\right)$$

$$Z = n_A n_B \sigma_{AB} \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

$$E_a = 5.77 \text{ eV}$$

$$\sigma_{AB} = 1$$

$$T = T_e$$

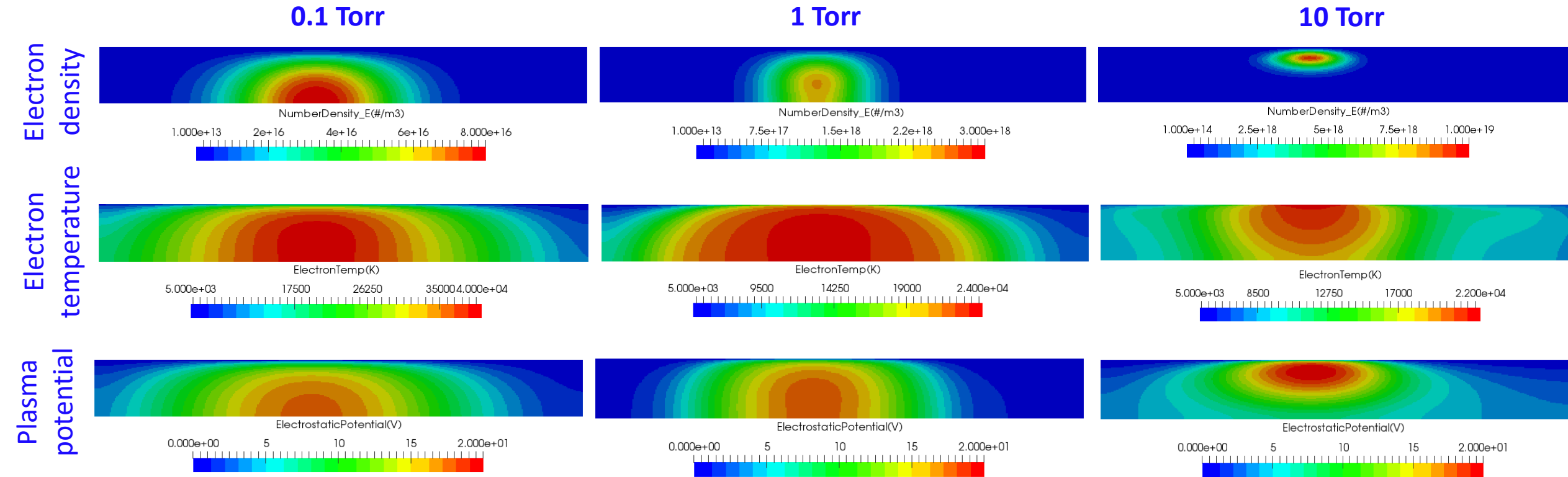
} Ionization of Ce (REE surrogate)

[1] Lay, B., Moss, R. S., Rauf, S. and Kushner, M. J., "Breakdown processes in metal halide lamps", Plasma Sources Science and Technology, No. 12, 2003, pp. 8-21.

[2] Bringer A., "4f – Ionization of Atomic Cerium", Solid State Communications, Vol.46, No.8, pp 591-593, 1983.

Plasma parameters for varying pressures

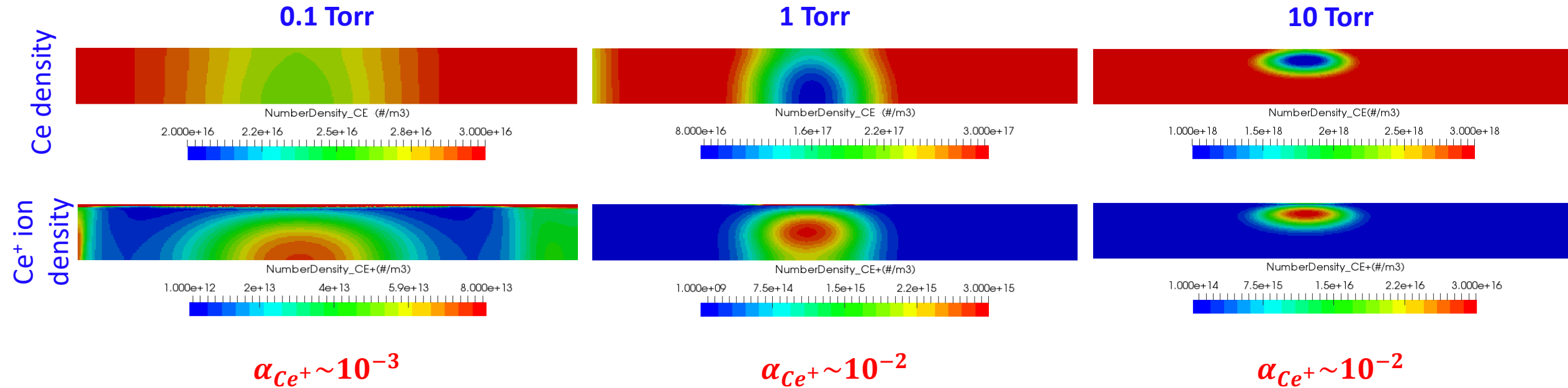
(pure argon carrier gas for trace 10^{-5} mole fraction RRE)



- Constant power in all cases
- Increasing plasma density with increasing pressure (anticipate higher throughput for RRE ionization)
- Plasma self constriction for increasing power (anticipate increased slip of unionized RRE)

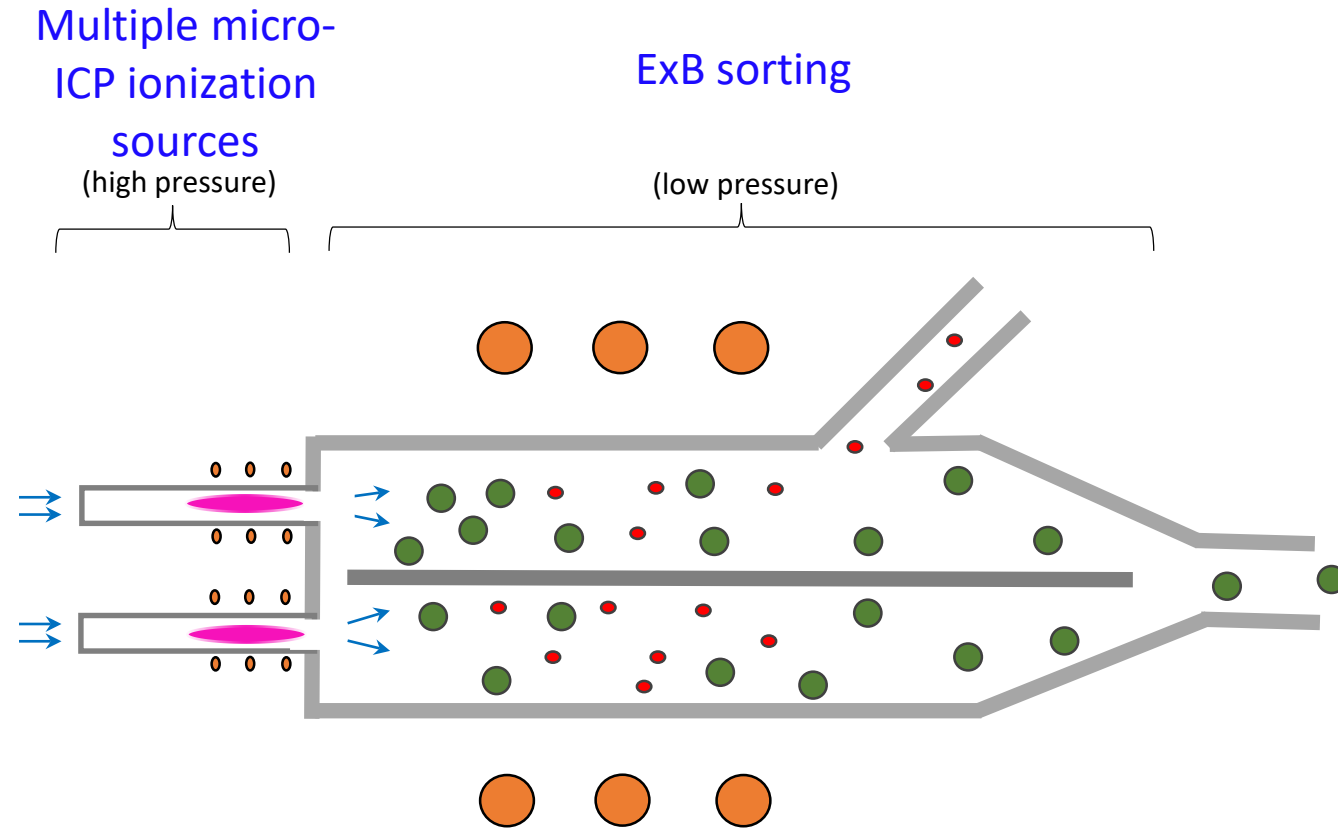
REE ionization for varying pressures

(pure argon carrier gas for trace 10^{-5} mole fraction RRE)

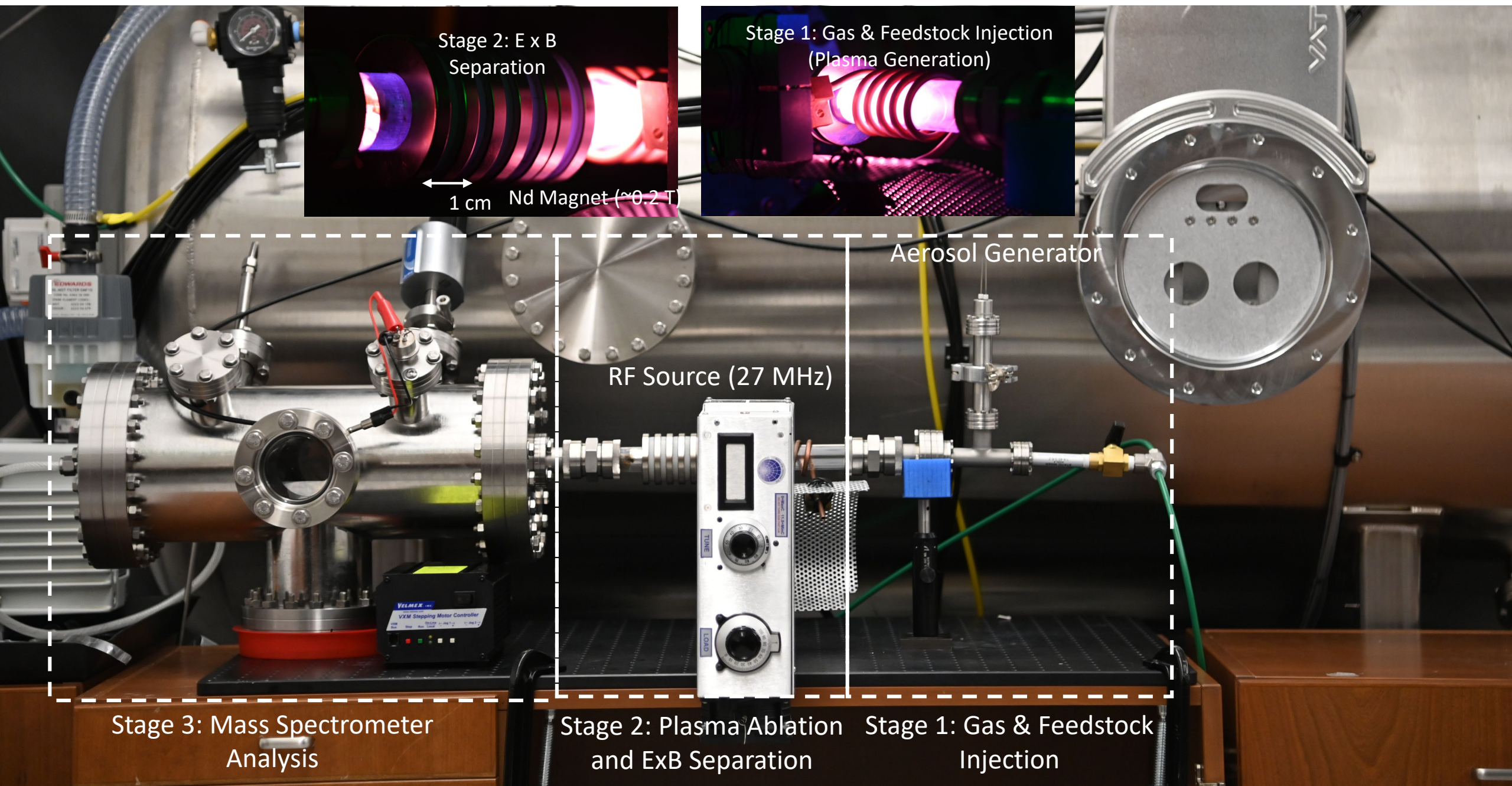


- Peak REE ionization fraction α_{Ce^+} increases for increasing pressures but saturates above 1 Torr
- Ions are quenched rapid at walls downstream of ionization region
- Plasma constriction at the highest pressure of 10 Torr results in significant slip/bypass of unionized Ce
- Hence, optimal pressure is ~ 1 Torr

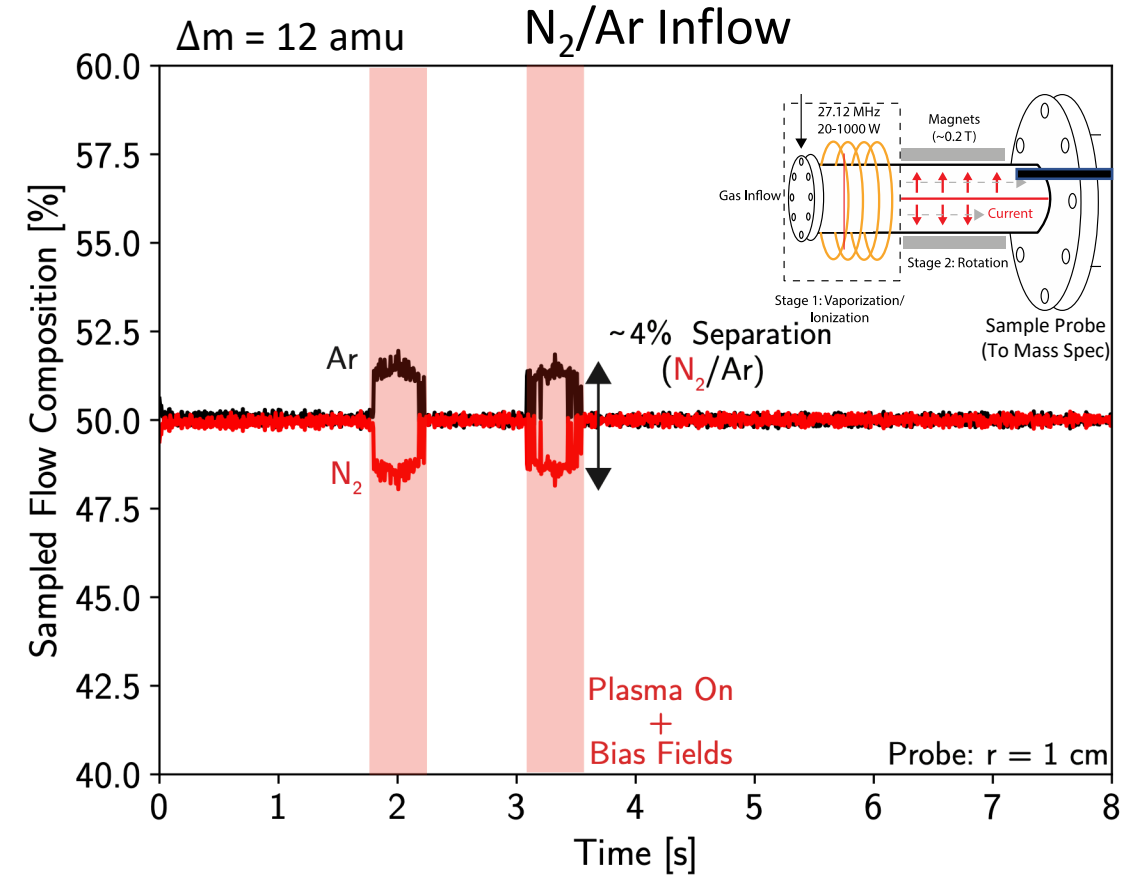
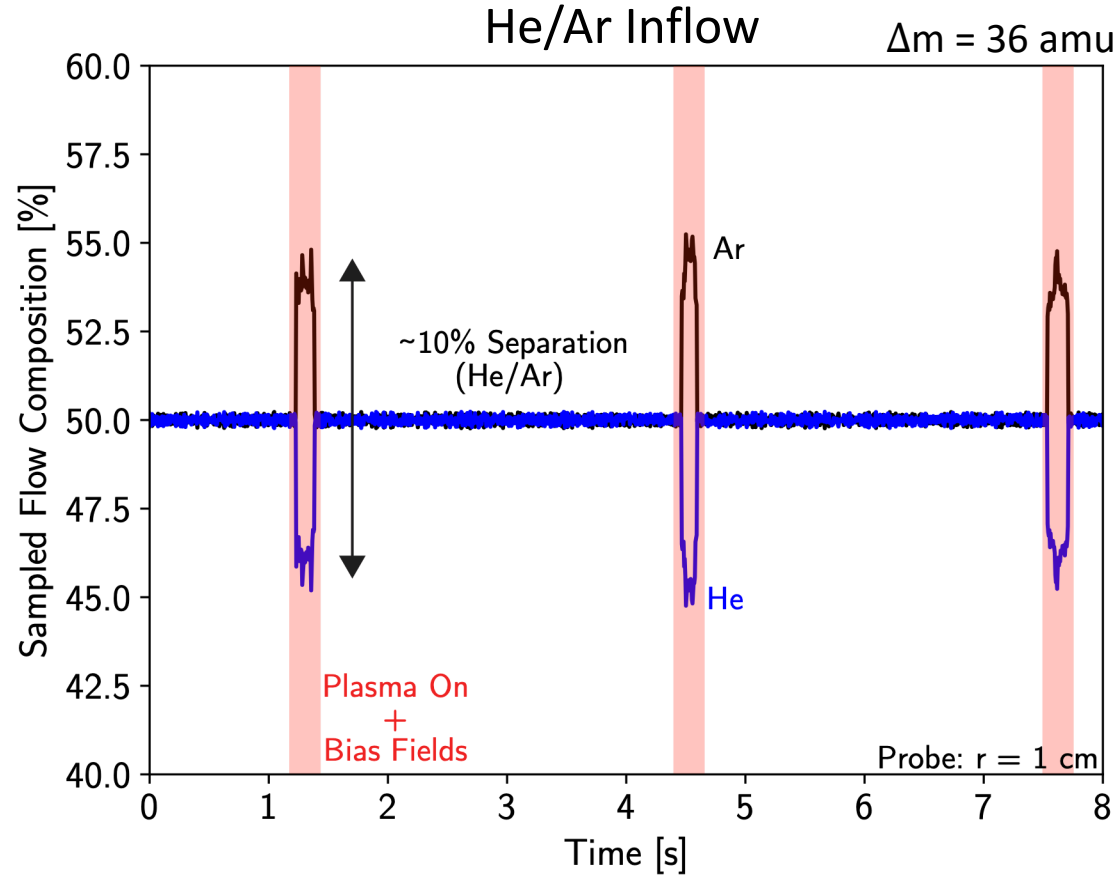
Rethink of original concept based on modeling insights



- Operate ICP ionizer at ~ 1 Torr
- Place ICP ionization zone immediately upstream of exit (REE ions are frozen immediately as they evacuate into *ExB* sorting region)



Separation of Gas Streams



Reaction Conditions:

- $P_{in} = 100$ W
- Residence Time = 0.1 ms
- Pressure = 200 mTorr
- Flow Rate = 50 sccm
- $B = 0.2$ T, $V = 100$ V

Advantages:

- Scalable to High Flow Rates
- Scalable to Collisional Pressures
- Fast Separation (~ 0.1 ms)
- Separation Dependent on Δm

Room for Optimization:

- Residence Time
- Position of Centrifuge
- Process Efficiency ($\gg 10$ eV/Separated Molecule)
- Vaporization

Acknowledgements

- Sheila Gerardo
- Navheen Murugesan
- Staci Loewy
- Nate Miller



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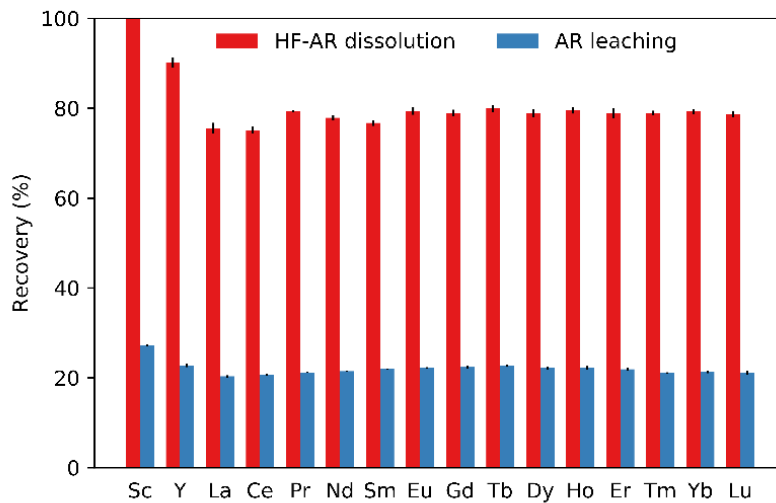


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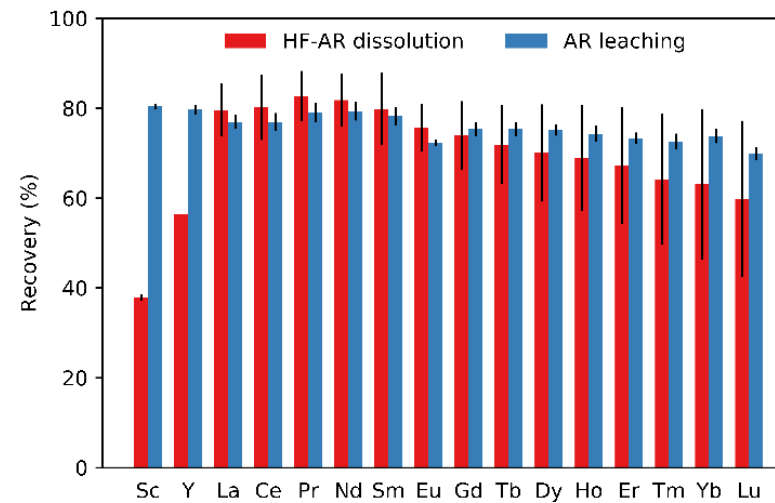


Acid Extraction Recovery Efficiencies

Illinois



Green River



Powder River

