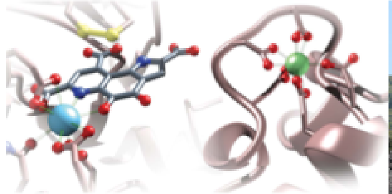
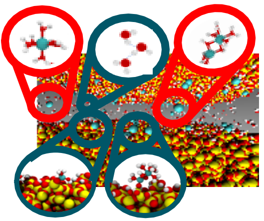
SAND2022-7867C

Bio-Inspired Harvesting of Rare Earth Metals





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TechConnect World Innovation Conference & Expo

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A Three-Part Tale

Bio-Inspired Harvesting of Rare Earth Metals

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Justin Gourary (UT Austin)

Nanoconfinement-driven capture of lanthanides

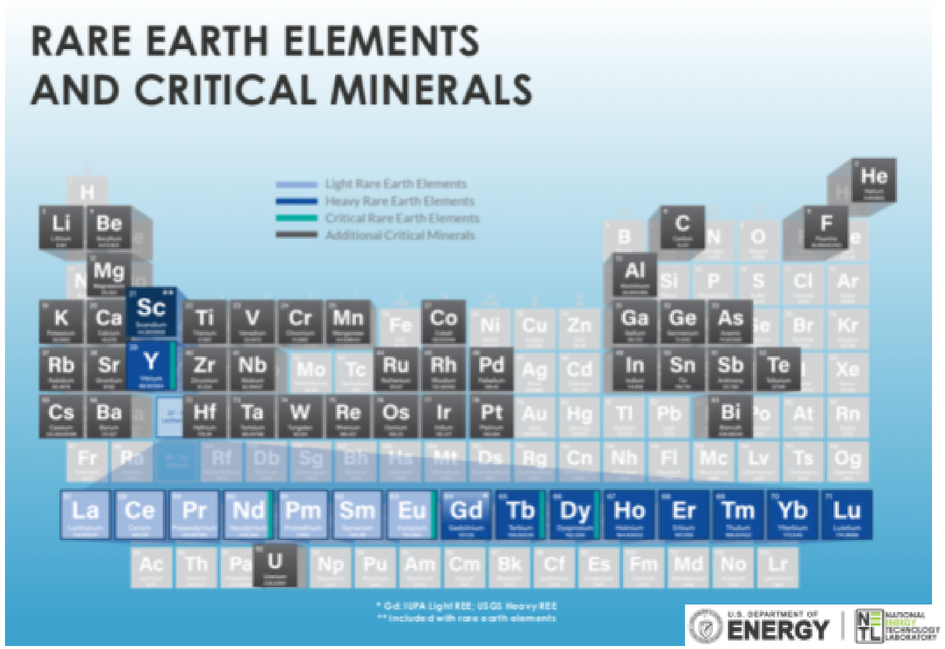
Anastasia Ilgen*
Kevin Leung
Louise Criscenti

Nadine Kabengi (Georgia State U.)

Environmentally Benign Extraction of Rare Earth Metals

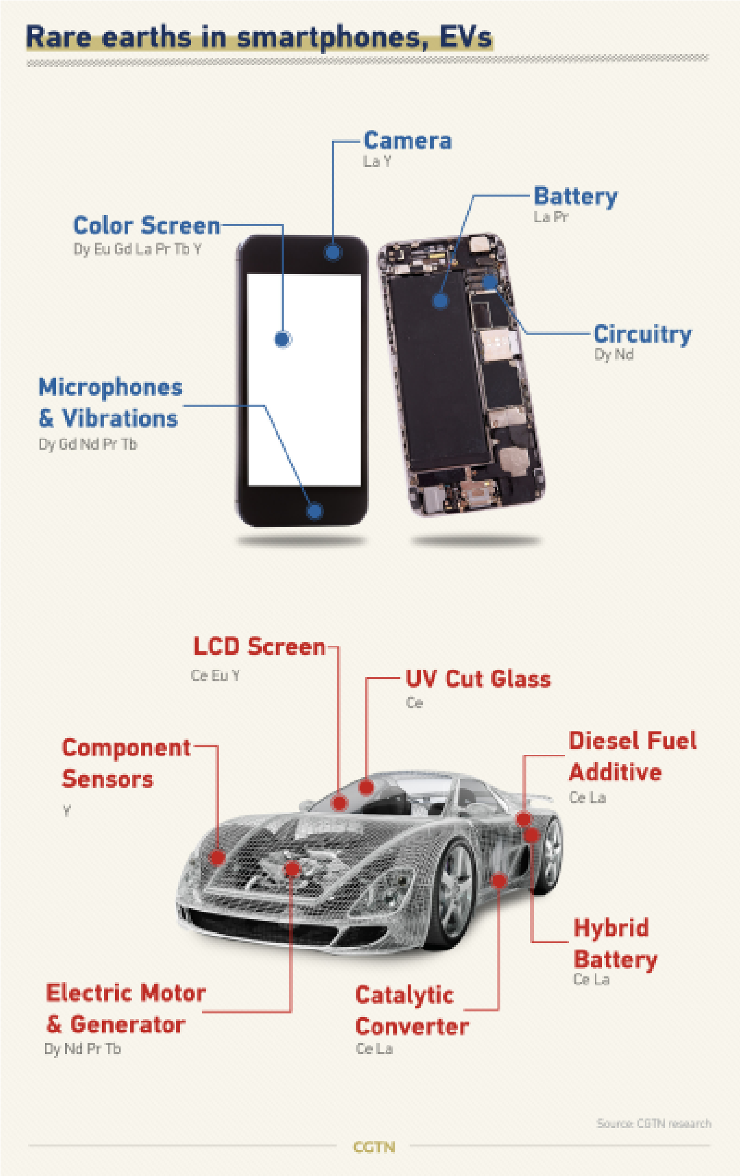
Guangping Xu*
Yongliang Xiong
Yifeng Wang
Mark Rigali

Rare Earths Metals (REMs) Are Technologically Important



Rare earth metals (REMs; lanthanides plus yttrium and scandium) are critical materials:

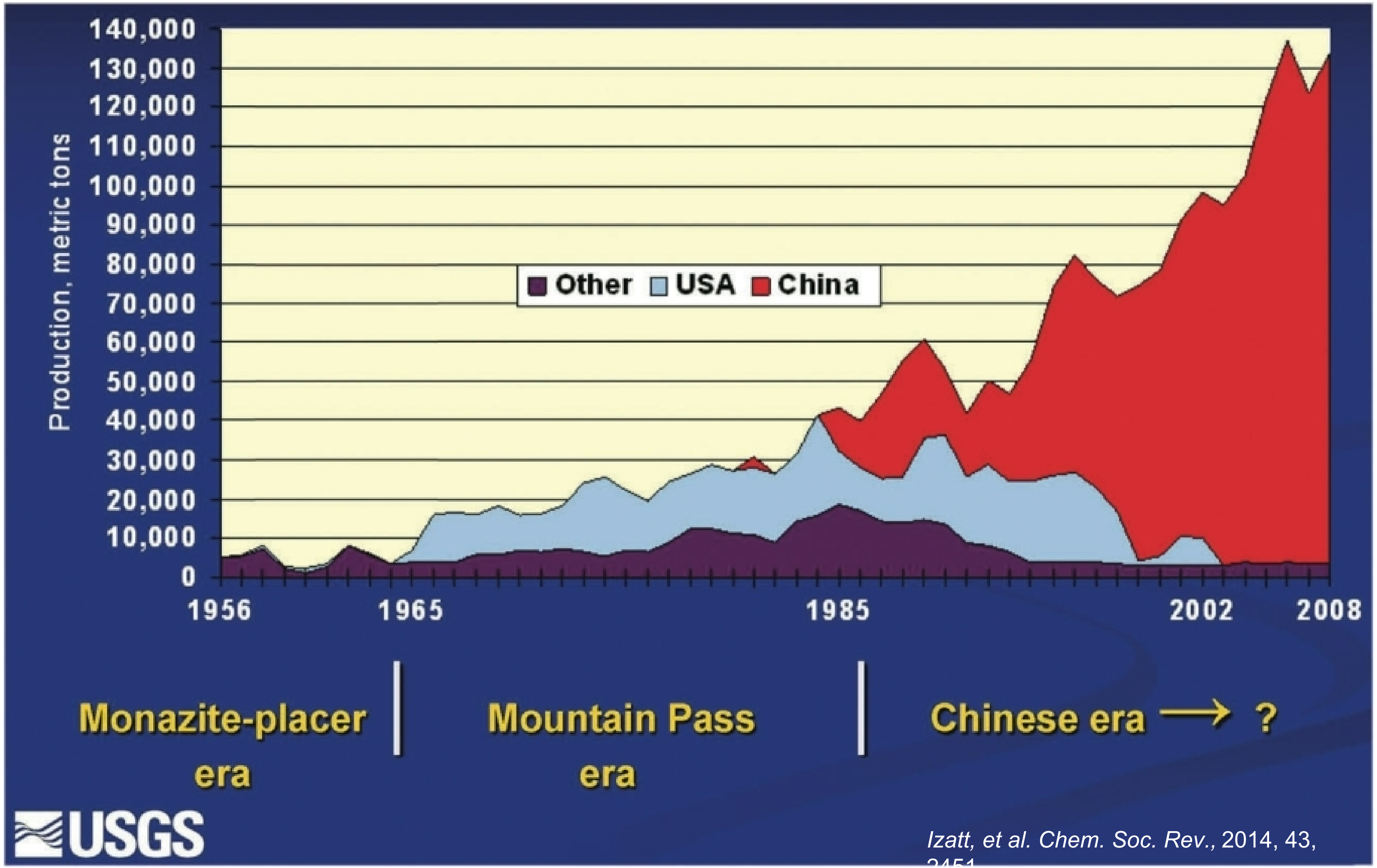
- telecommunications,
- energy infrastructure and renewable energy
- lighting
- medical technologies,
- defense technologies
- other essential advanced systems.



Source: CGTN research

Where Do We Get REMs?

The U.S. was once a leader in REM mining and production…



Izatt, et al. Chem. Soc. Rev., 2014, 43, 2451

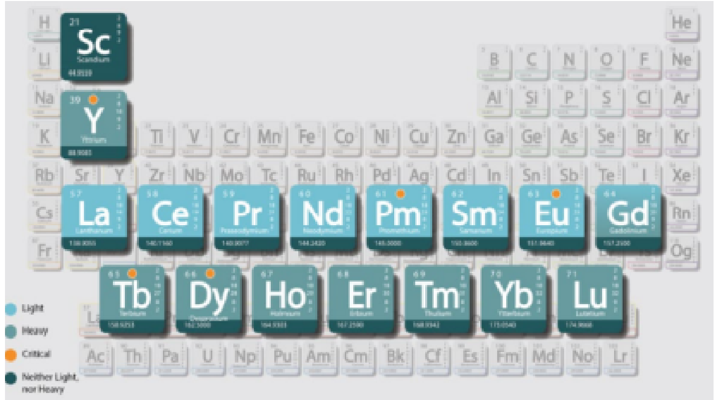
Where Do We Get REMs?

Today, the U.S. relies on 100% import for many critical minerals.

Mineral Commodity	2019 U.S. net import reliance	Top Producer	Mineral Commodity	2019 U.S. net import reliance	Top Producer
arsenic	100%	China	**barite**	87%	China
cesium	100%	Canada	**antimony**	84%	China
fluorspar	100%	China	**rhenium**	82%	Chile
gallium	100%	China	**cobalt**	78%	Congo
graphite (natural)	100%	China	**tin**	77%	China
indium	100%	China	**aluminum (bauxite)**	>75%	China
manganese	100%	China	**chromium**	>75%	South Africa
niobium	100%	Brazil	**platinum group**	64%	South Africa
rare earth group	100%	China	**magnesium**	52%	China
rubidium	100%	Canada	**germanium**	>50%	China
scandium	100%	China	**tungsten**	>50%	China
strontium	100%	Spain	**lithium**	>25%	Australia
tantalum	100%	Rwanda	**beryllium**	<21%	U.S.
bismuth	96%	China	**hafnium**	n.d.	Australia
tellurium	>95%	China	**uranium**	n.d.	Kazakhstan
vanadium	94%	China	**helium**	net exporter	U.S.
titanium	93%	China	**zirconium**	net exporter	Australia
potash	91%	Canada			

n.d. not enough information to calculate the import reliance

USGS Mineral Commodity Summaries 2020



Rare Earth Metals (REE)

Critical:
Nd, Tb, Dy, Eu, Y, Er, Pr

Uncritical: La, Sm, Gd

Excessive (supply > demand):
Ce, Ho, Tm, Yb, Lu

REM Harvesting Challenges

REMs are:

- Naturally dilute
- Found in complex mixtures
- Similar charge, size, and chemistry

Current methods:

- Thousands of mixer-settler tanks
- Energy & chemically-intensive
- Large ammonia consumption
- ***Toxic, carcinogenic and hazardous to aquatic life/environment.***

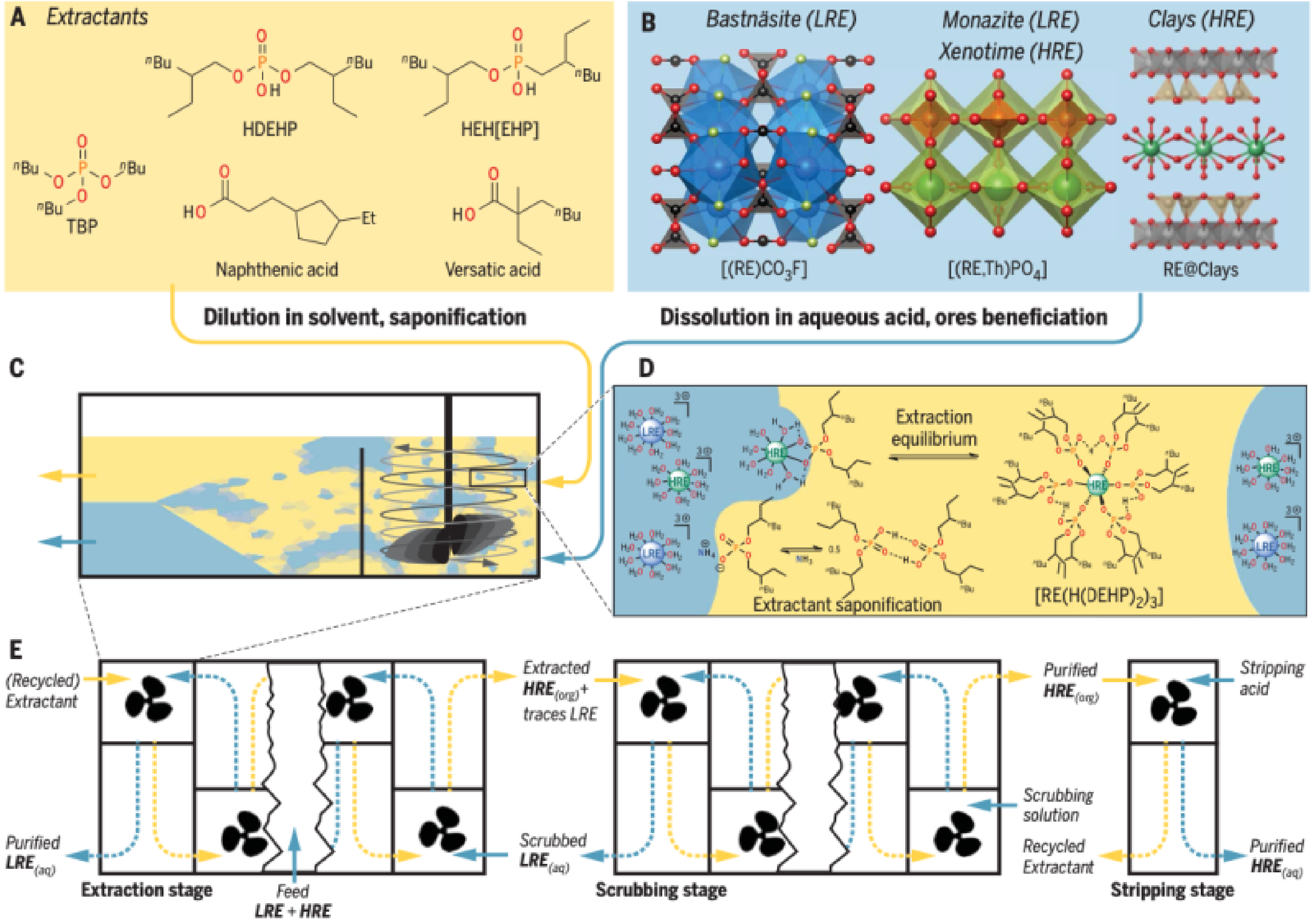


Fig. 2. Solvent extraction. (**A**) Commonly used extractants. (**B**) Typical RE-containing minerals. (**C**) Cut-off side view of a simple mixer-settler unit. (**D**) Schematic extraction equilibria. (**E**) Flow chart (top view) of batteries of mixer-settlers in a model industrial process with extraction, scrubbing, and stripping stages.

Cheisson, T. & Schelter, E. J. Rare earth elements: Mendeleev's bane, modern marvels. *Science* **363**, 489-493 (2019).

Transforming Coal-based Resources to Produce Critical Minerals

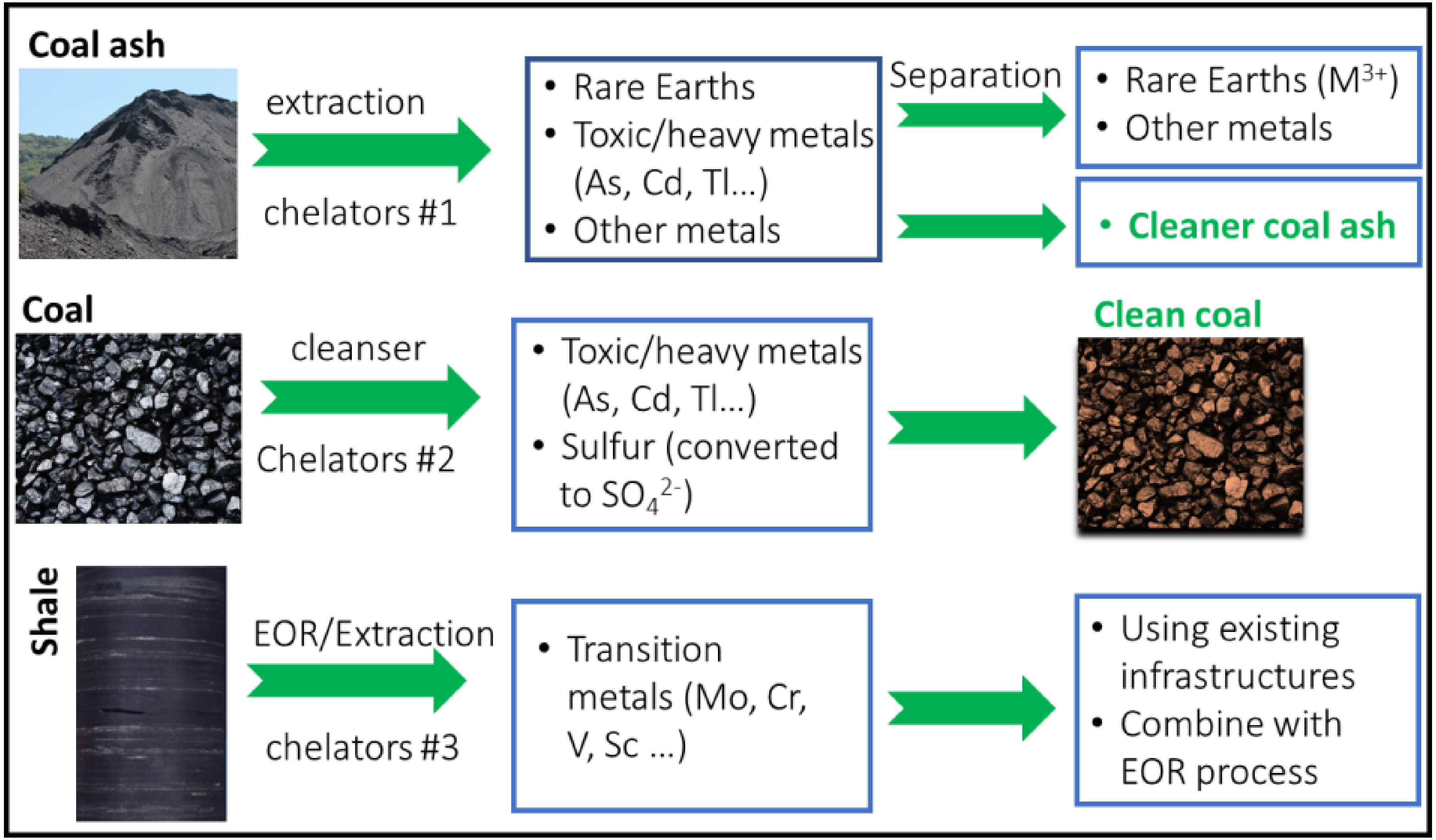
| Guangping Xu, Ph. D. | Geochemistry Department | Sandia National Laboratories | gxu@sandia.gov|

Recover critical metals and toxic metals from domestic resources (coal/coal byproduct/shale)

1. **Critical mineral sustainability requirement**
   - U.S. has vast natural resources of coal and shale, enough for hundreds of years of use.
   - Many coal seam, coal ash and shale intervals have REE contents that are more enriched than 20-40% conventional ore deposits
2. **Environmental sustainability requirement**
   - 3 billion tons of existing coal ash "polluting and causing damage" to the environment, additional tens of million tons generated annually
   - Coal ash is hazardous but not regulated as such, and EPA is proposing to regulate coal ash
   - Current extracting technologies using strong acids/bases, converting solid wastes into more hazardous solution waste
3. **Transforming vast natural resources of coal and shale to nonfuel Carbon-Based Products (CBP)**
   - Important to remove toxic metals in order for coal to repurpose CBPs

Sourcing Rare Earths Domestically

Three main domestic resources to recover critical metals and toxic metals



Coal ash

extraction

chelators #1

- Rare Earths
- Toxic/heavy metals (As, Cd, Tl...)
- Other metals

Separation

- Rare Earths (M^{3+})
- Other metals

- **Cleaner coal ash**

Coal

cleanser

Chelators #2

- Toxic/heavy metals (As, Cd, Tl...)
- Sulfur (converted to SO_4^{2-})

Clean coal

Shale

EOR/Extraction

chelators #3

- Transition metals (Mo, Cr, V, Sc ...)

- Using existing infrastructures
- Combine with EOR process

Guangping Xu

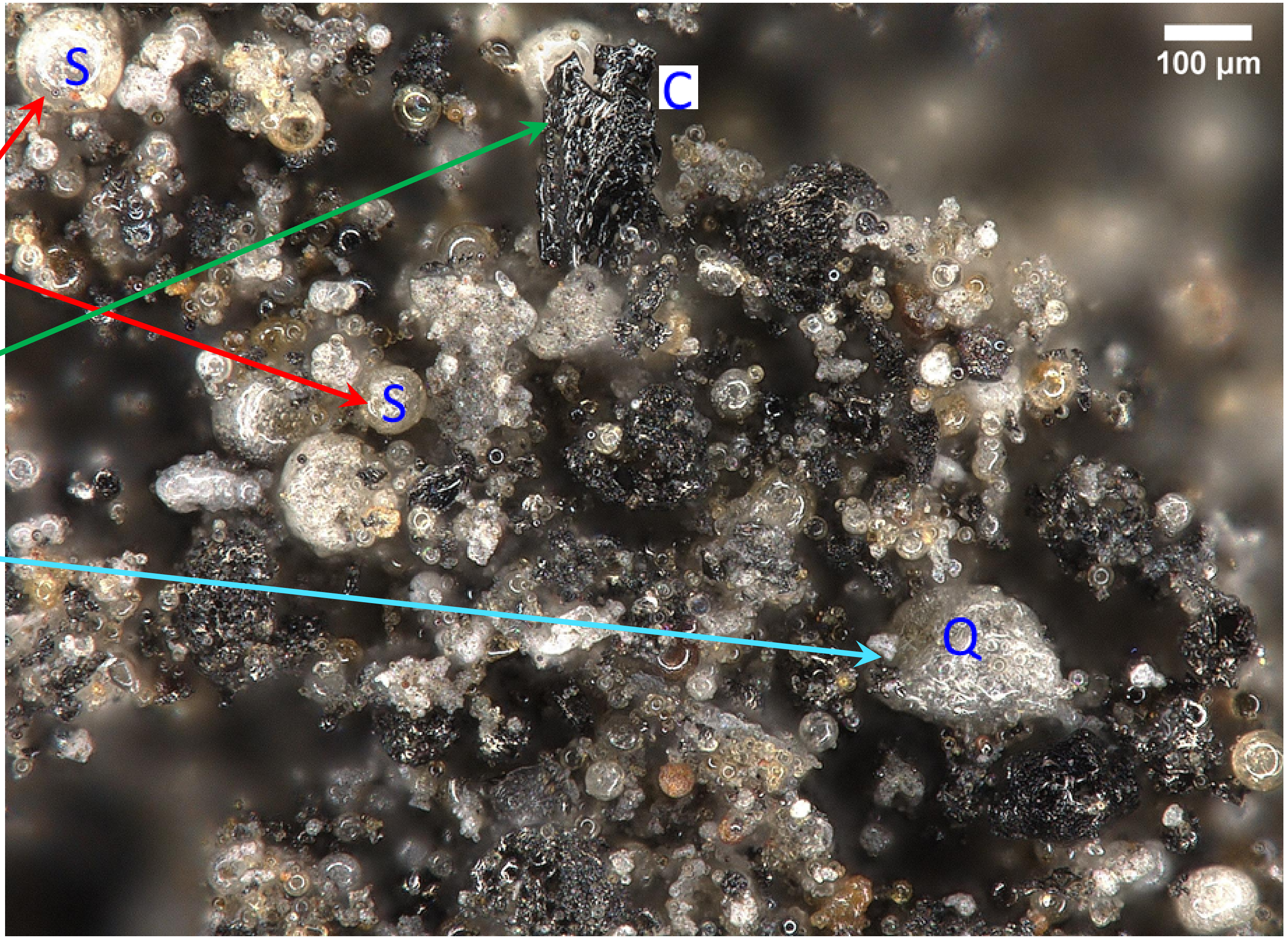
Finding Critical Materials in Coal Ash

Thera are several critical metal hosting phases in coal ash:

Amorphous silicate glass sphere (**S**)

Residual carbon (**C**)

Accessory minerals (monazite, xenotime, quartz (**Q**) etc.)

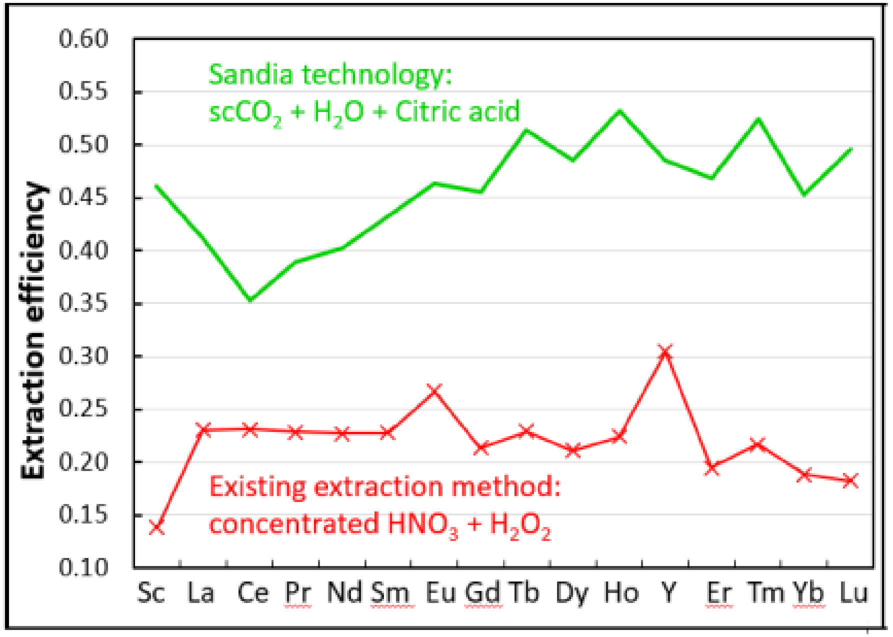


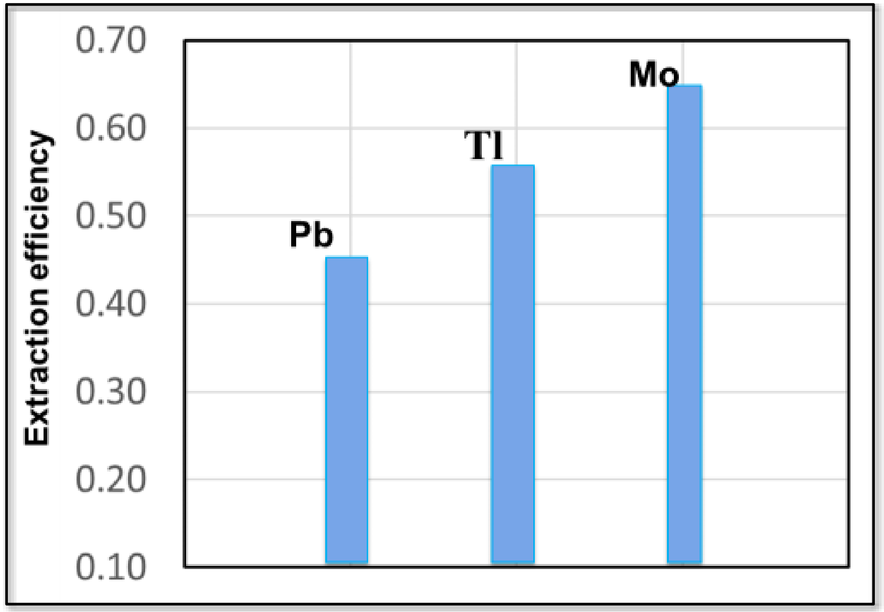
- ~40% entrenched inside glass sphere;
- ~60% critical metals are hosted in other phases.

Guangping Xu

Research Approach: $scCO_2$ + chelator + H_2O system

1. Supercritical CO_2 ($scCO_2$) is an excellent solvent.
2. Citric acid is an acid and also an excellent chelating agent.





- More than 50% heavy rare earths extracted without using strong acids/base
- 45 – 65% toxic/heavy metals were also removed, resulting in cleaner coal / coal ash for reuse

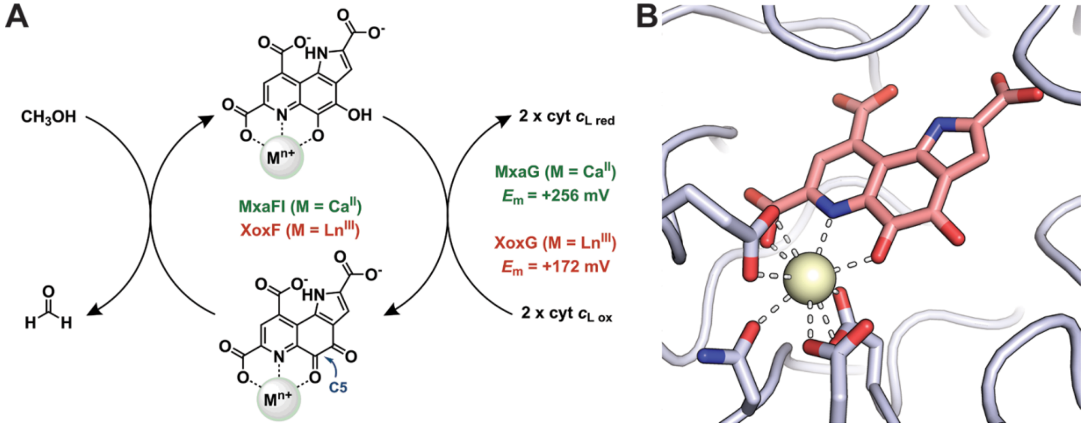
2021 R&D 100 Award: Gold Medal (1st Place) Special Recognition for Green Tech

Guangping Xu

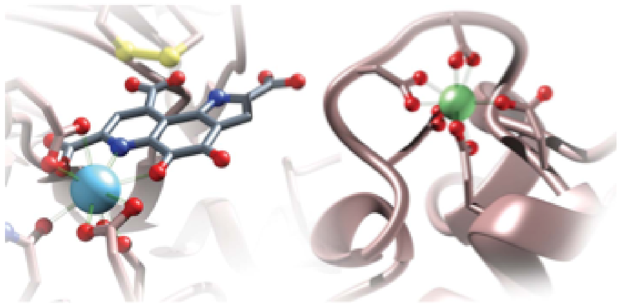
Selective Bio-Inspired Harvesting of Rare Earth Metals

Biological Systems Have Created a Solution…

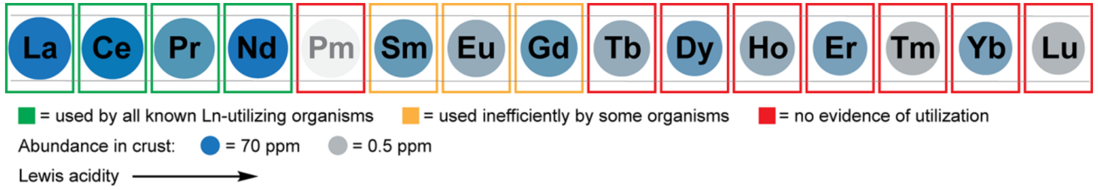
Methyltrophic bacteria, which rely on the catalytic conversion of methanol as a primary carbon and energy source, *depend on highly-selective binding* of lanthanide (LN)-group REMs to enable these critical catalytic processes.



J.A. Cotruvo, *ACS Cent. Sci*. 2019, **5**, 1496



Cheisson, T. & Schelter, E. J. *Science* **363**, 489-493 (2019).

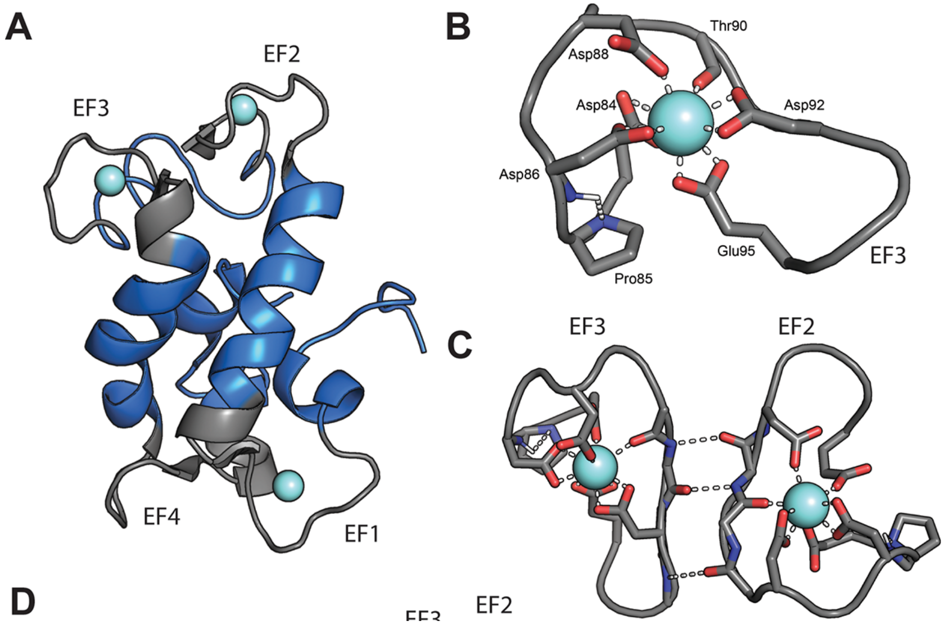


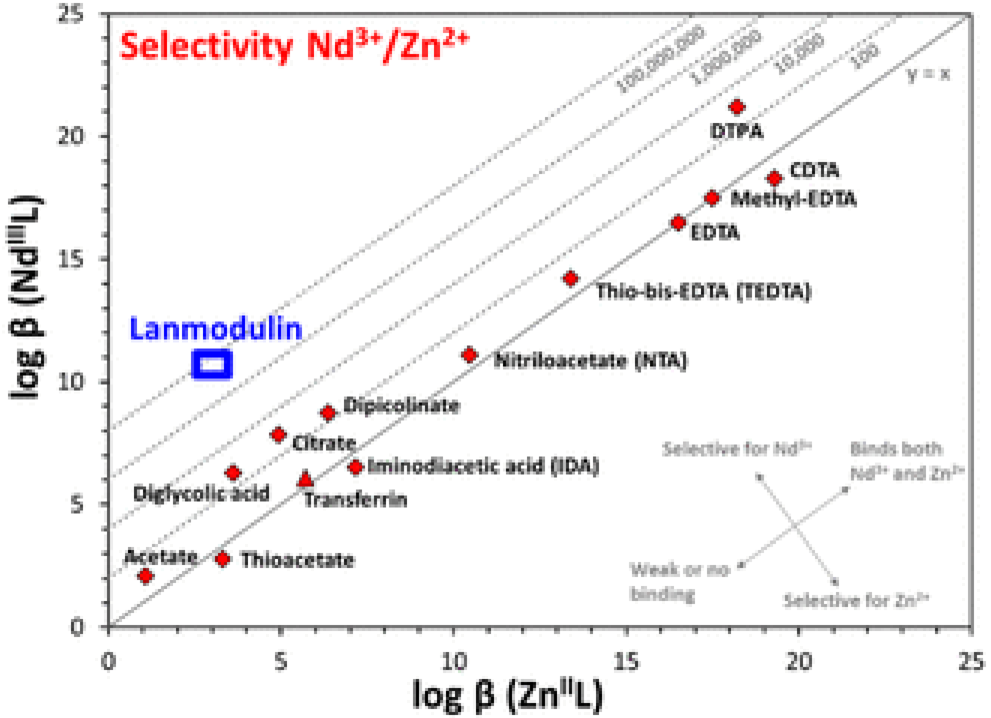
🟩 = used by all known Ln-utilizing organisms 🟧 = used inefficiently by some organisms 🟥 = no evidence of utilization

Abundance in crust: ● = 70 ppm ● = 0.5 ppm

Lewis acidity →

Lanmodulin (LanM) has remarkable REM Binding Selectivity





LanM has been shown to have a strong affinity, (K_d ~1-10 pM for a range of lanthanides, compared to ~1 mM for Ca^{2+}).

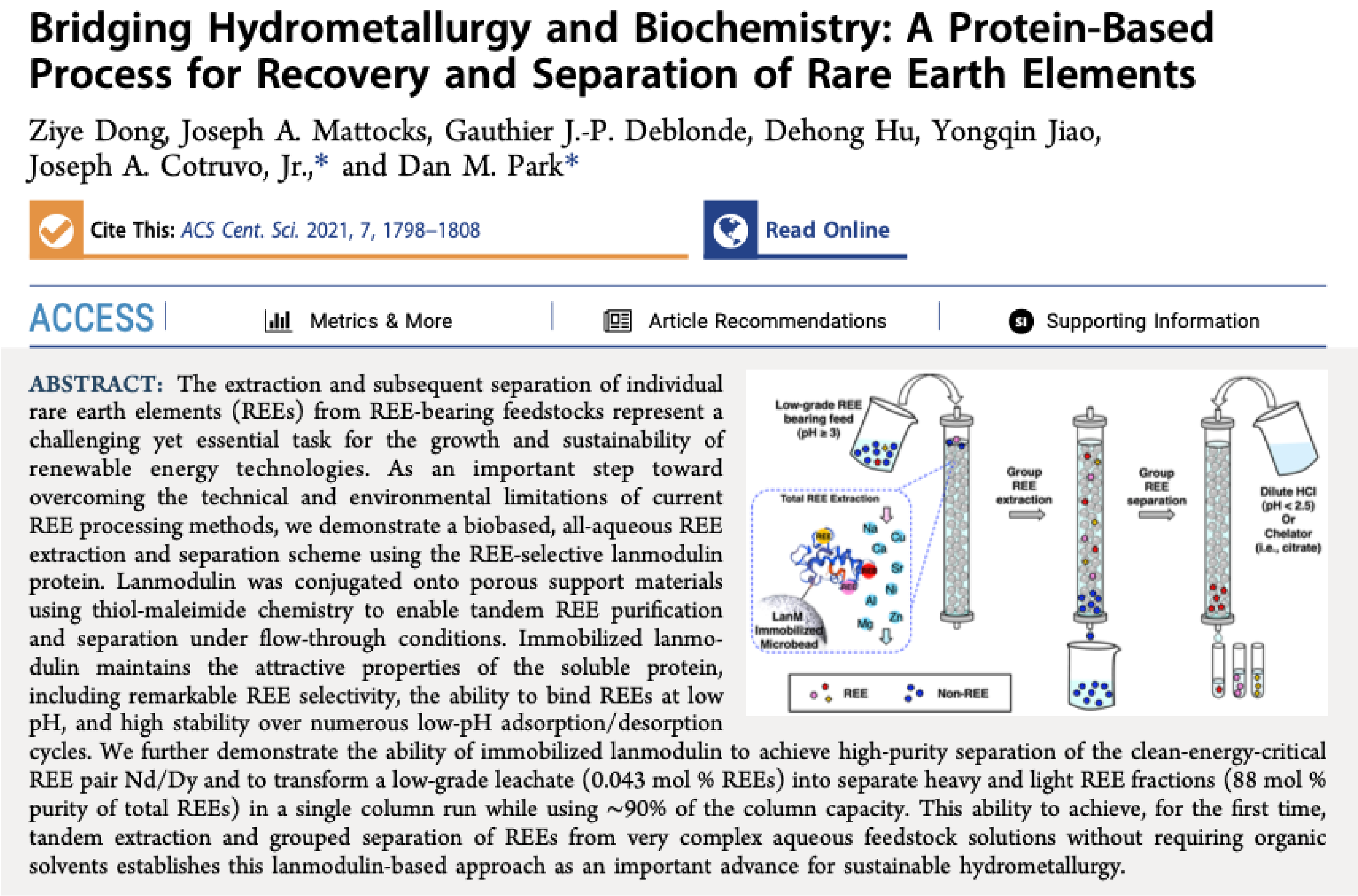
“REE/non-REE selectivity of LanM is orders of magnitude higher than most small molecules or macromolecules ever studied.” - Deblonde, et al.

We hypothesize *that specific compositional and structural properties of biological ligands that govern selective interactions with solubilized REMs can be distilled to inform synthetic bio-inspired analogs for REM extraction and separation.*

Deblonde, G. J. P. *et al.* Selective and Efficient Biomacromolecular Extraction of Rare-Earth Elements using Lanmodulin. *Inorganic Chemistry* **59**, 11855-11867, (2020).

Progress Toward Engineered LanM REM Harvesting

Coupling LanM to solid supports enables efficient REM extraction and separation!



Bridging Hydrometallurgy and Biochemistry: A Protein-Based Process for Recovery and Separation of Rare Earth Elements

Ziye Dong, Joseph A. Mattocks, Gauthier J.-P. Deblonde, Dehong Hu, Yongqin Jiao, Joseph A. Cotruvo, Jr.,* and Dan M. Park*

Cite This: *ACS Cent. Sci.* 2021, 7, 1798−1808

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ABSTRACT: The extraction and subsequent separation of individual rare earth elements (REEs) from REE-bearing feedstocks represent a challenging yet essential task for the growth and sustainability of renewable energy technologies. As an important step toward overcoming the technical and environmental limitations of current REE processing methods, we demonstrate a biobased, all-aqueous REE extraction and separation scheme using the REE-selective lanmodulin protein. Lanmodulin was conjugated onto porous support materials using thiol-maleimide chemistry to enable tandem REE purification and separation under flow-through conditions. Immobilized lanmodulin maintains the attractive properties of the soluble protein, including remarkable REE selectivity, the ability to bind REEs at low pH, and high stability over numerous low-pH adsorption/desorption cycles. We further demonstrate the ability of immobilized lanmodulin to achieve high-purity separation of the clean-energy-critical REE pair Nd/Dy and to transform a low-grade leachate (0.043 mol % REEs) into separate heavy and light REE fractions (88 mol % purity of total REEs) in a single column run while using ~90% of the column capacity. This ability to achieve, for the first time, tandem extraction and grouped separation of REEs from very complex aqueous feedstock solutions without requiring organic solvents establishes this lanmodulin-based approach as an important advance for sustainable hydrometallurgy.

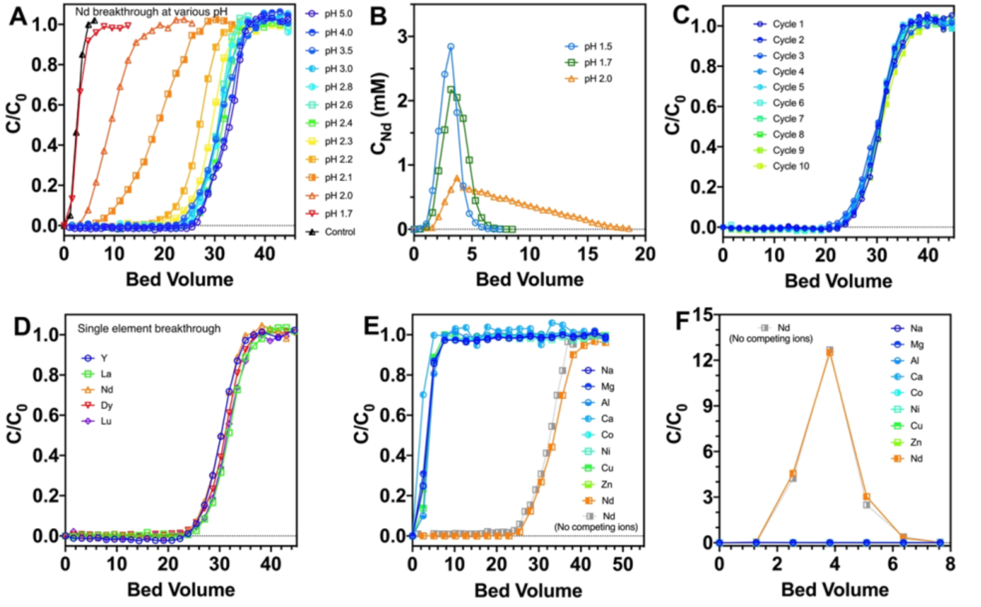
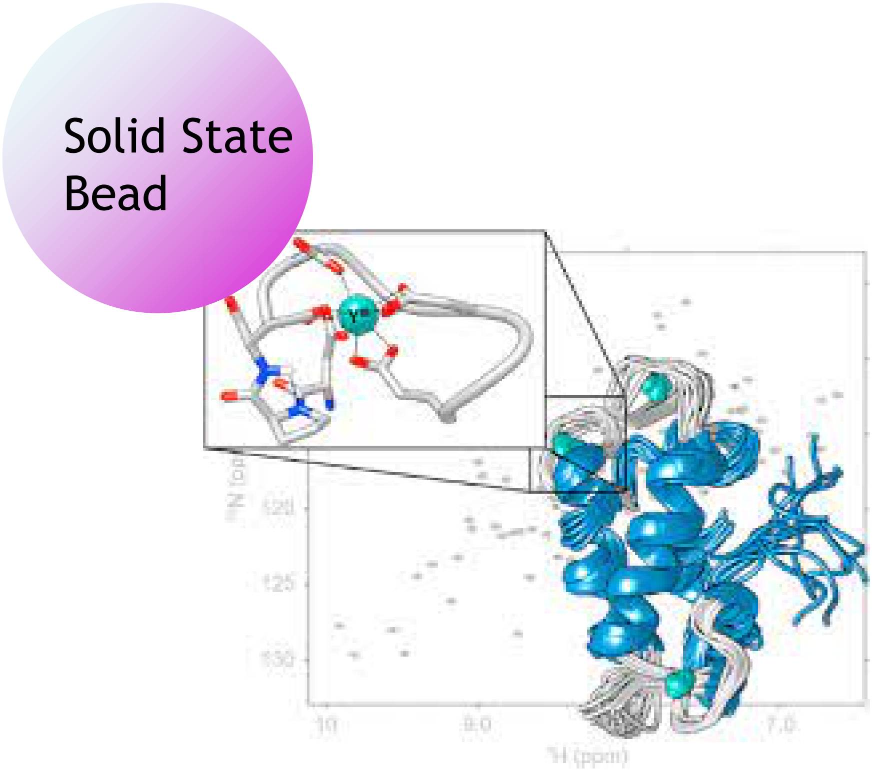
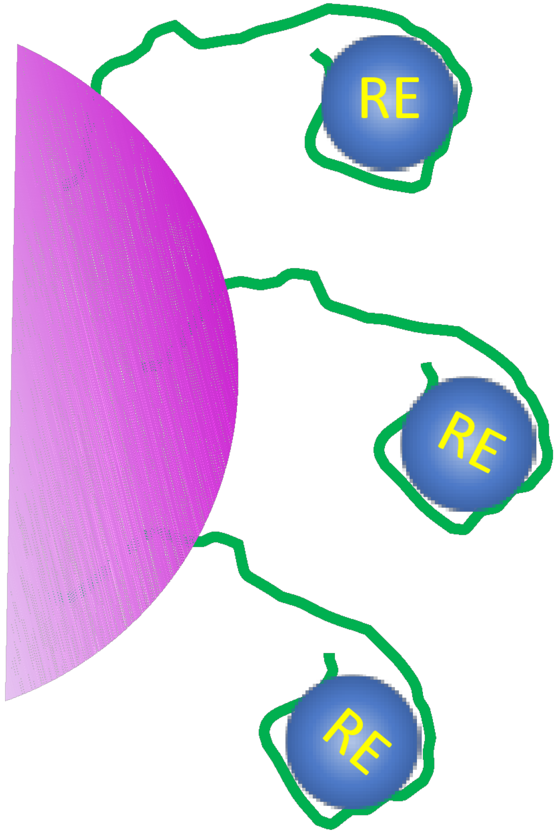


Figure 2. Immobilized LanM enables high-selectivity REE extraction at low pH.

Our Approach - A Two-Part Challenge



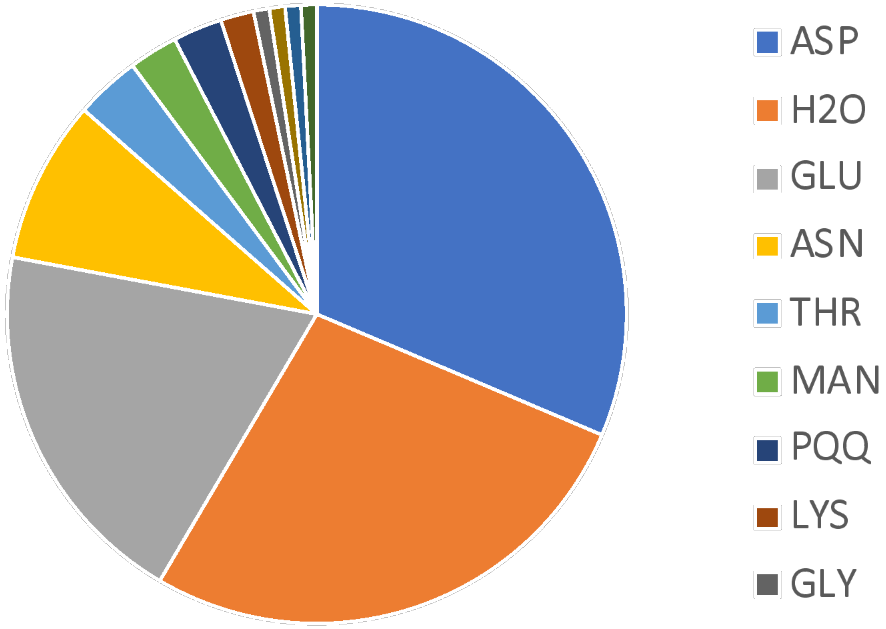
1. Can we identify specific compositional and structural properties of biological ligands that govern selective REM capture?
2. Can we incorporate these properties into synthetic ligands capable of scalable REM harvest and separation?



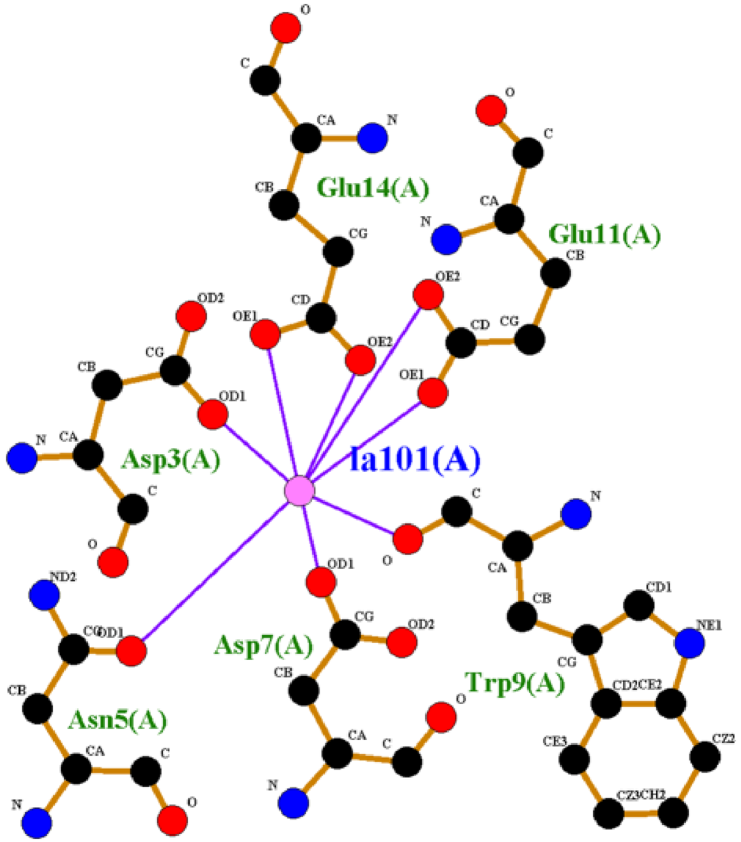
REBELS: Rare Earth Binding Engineered Ligand Supports

LanM images from Cook, et al. (2019) *Biochem*. **58**, 120-125.

Computational Modeling: Where to Start?



- 15 Lanthanum Containing PDB Structures
- 27 Valid Lanthanum Binding Sites
- 153 Binding Site Residues
- 5.9 Residues per Binding Site
- 7.8 Contacts per Binding Site



Binding Site from a Lanthanum Binding Tag protein (7CCO)

Natural REM binding structures are structurally complex, but share common ligand chemistries.

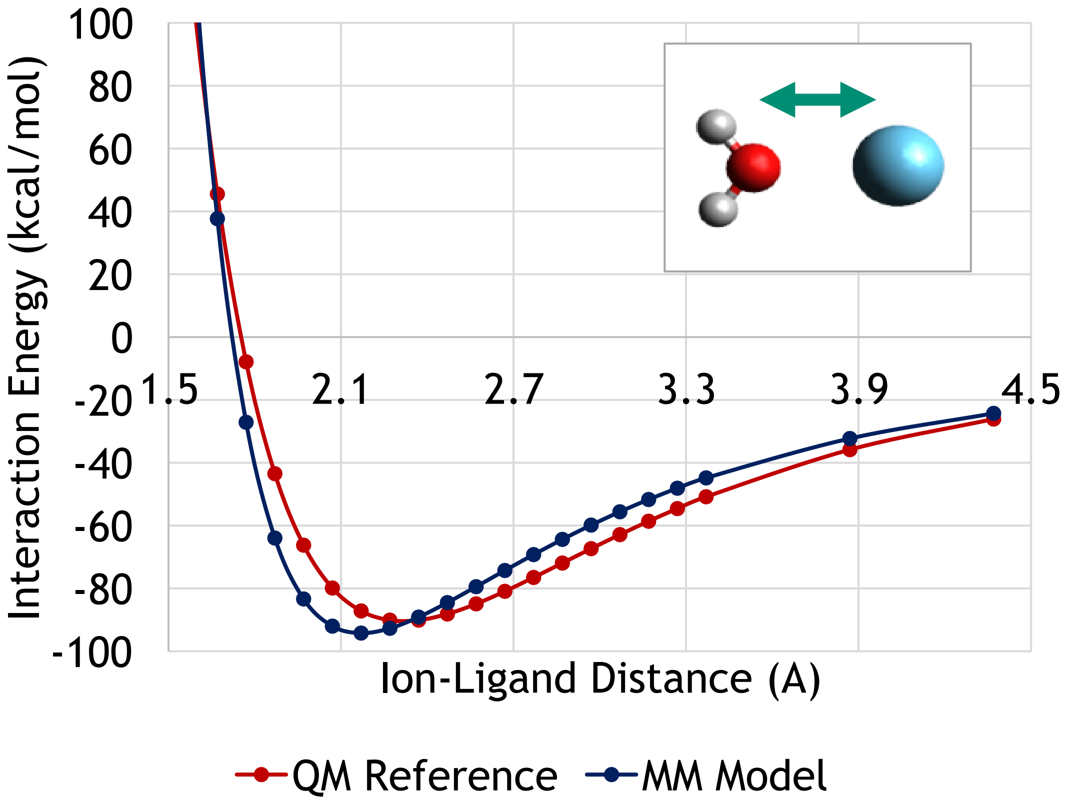
J. Gourary, P. Ren, and S. Rempe

Determining Ion Interaction and Hydration Energies

Using AMOEBA (Atomic Multipole Optimized Energetics for Biomolecular Applications)

- Incorporates atomic multipole electrostatics and electronic polarization (especially important for protein-ligand interactions)
- Offers more accurate description of electrostatic interactions and properties in complex physical and chemical environments
- Allows you to capture many-body interactions, important in protein binding

La-water interaction energy in AMOEBA vs QM using PSI4 with MP2/CBS (def2-[TQ]ZVPD) with CCSD(T) correction



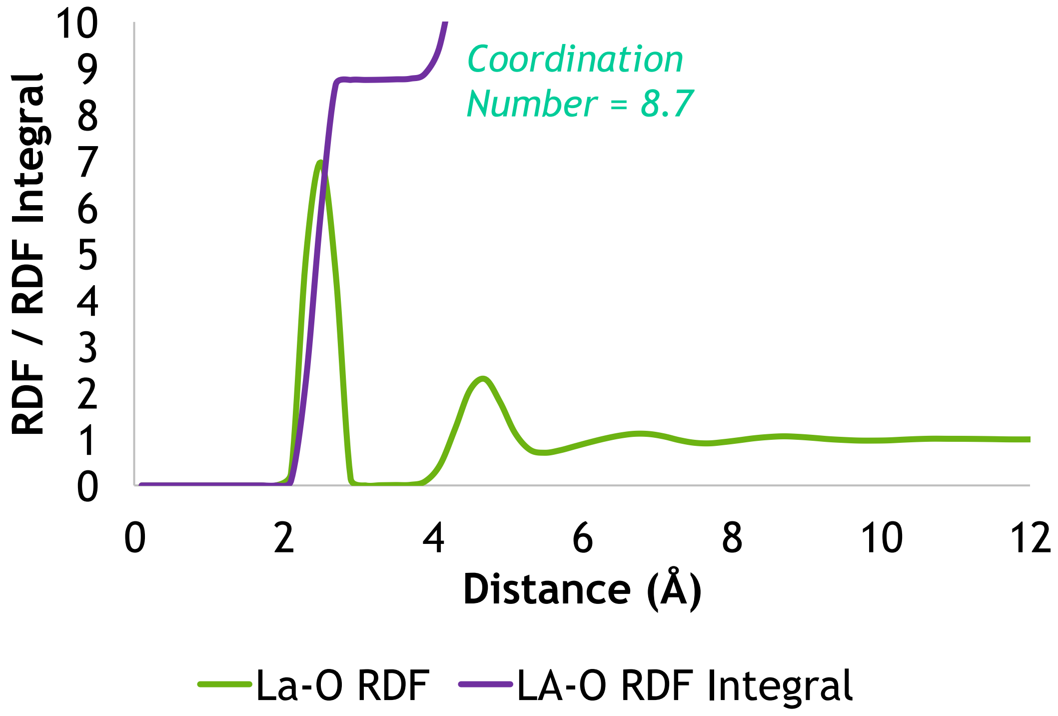
J. Gourary, P. Ren, and S. Rempe

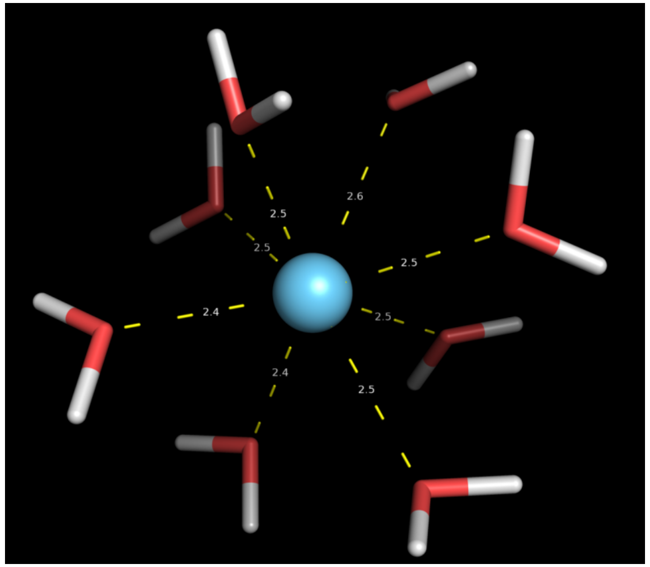
Effective AMOEBA model parameters (force fields) allow for an accurate calculation of hydration free energy.

	Hydration Free Energy (kcal/mol)
Experimental Reference	-746.66
MM Model	-740.02

Z. Jing, C. Liu, P. Ren “Many-body effect determines the selectivity for Ca^{2+} and Mg^{2+} in proteins.” (2018) *PNAS* **115** (32) E7495-E7501.

La-Solvation Structure Evolves





Example first shell of La^{3+} in water from an MD trajectory with distances displayed in angstroms (2.4-2.6Å).

Size decreases across the series

Coordination Number ~9

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
138.906	140.115	140.908	144.24	144.913	150.36	151.966	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967

Coordination Number ~8

1.032 Å

0.861 Å

Lowest hydration energy

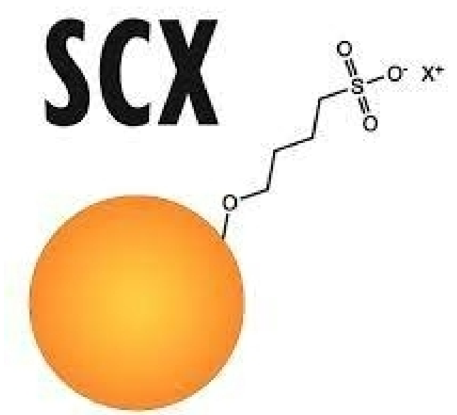
Highest hydration energy

J. Gourary, P. Ren, and S. Rempe

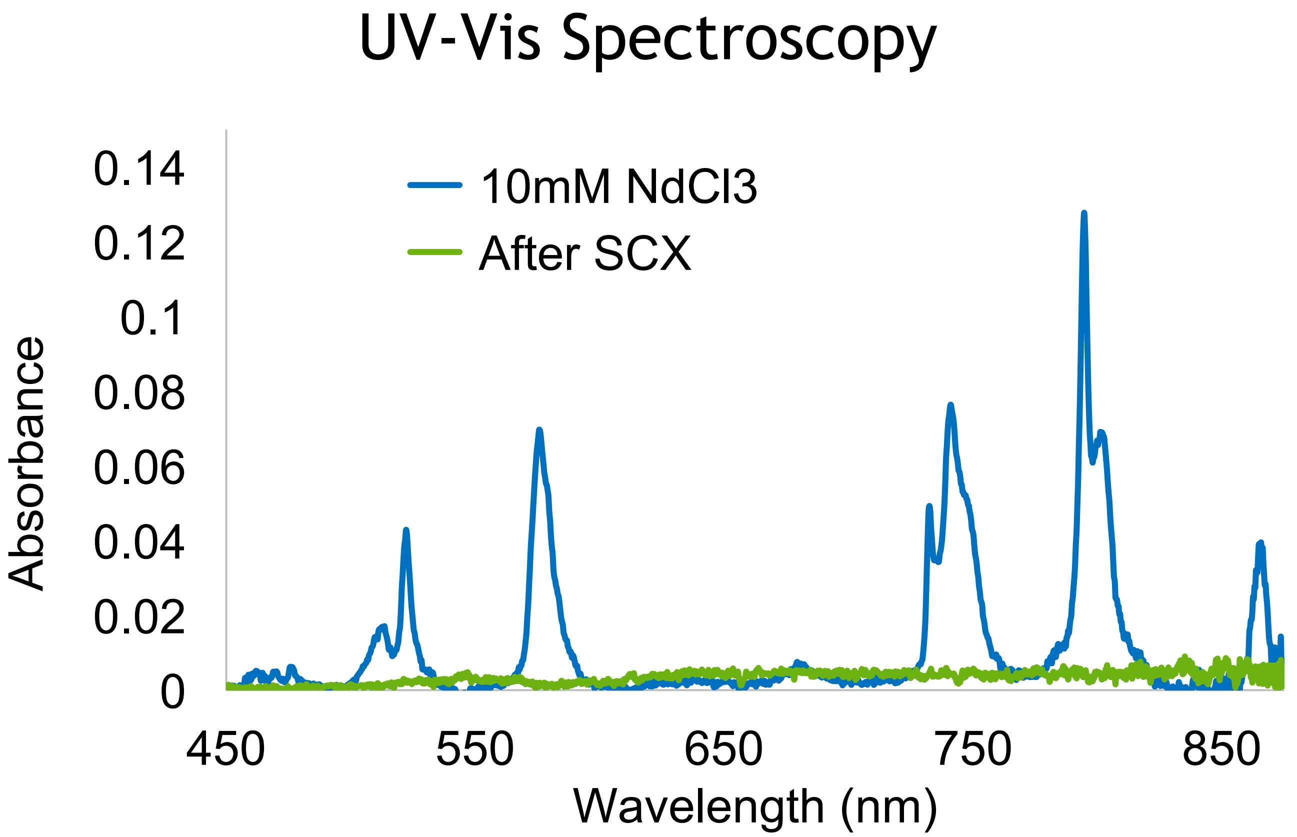
THE UNIVERSITY OF TEXAS AT AUSTIN

Proof of Principle REBELS Test

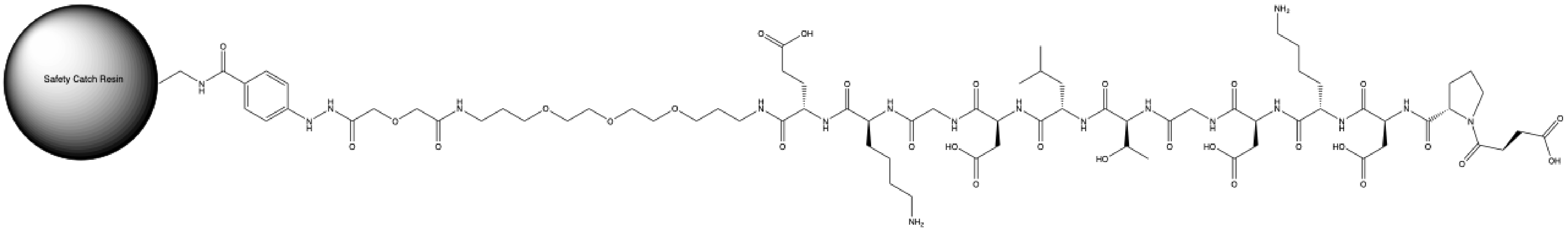
Flowing dissolved Nd^{3+} solution through commercial ion-exchange resin, showed feasibility of removing REM from solution.

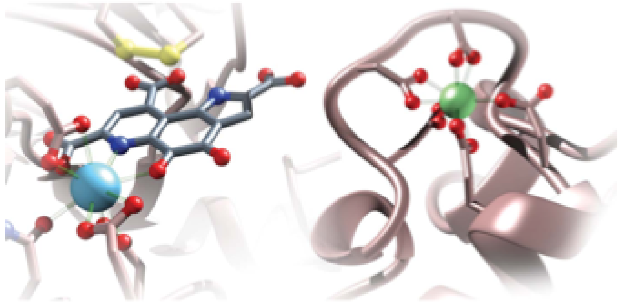


Burdick & Jackson strong cation exchange resin (sulfonic acids)


UV-Vis Spectroscopy

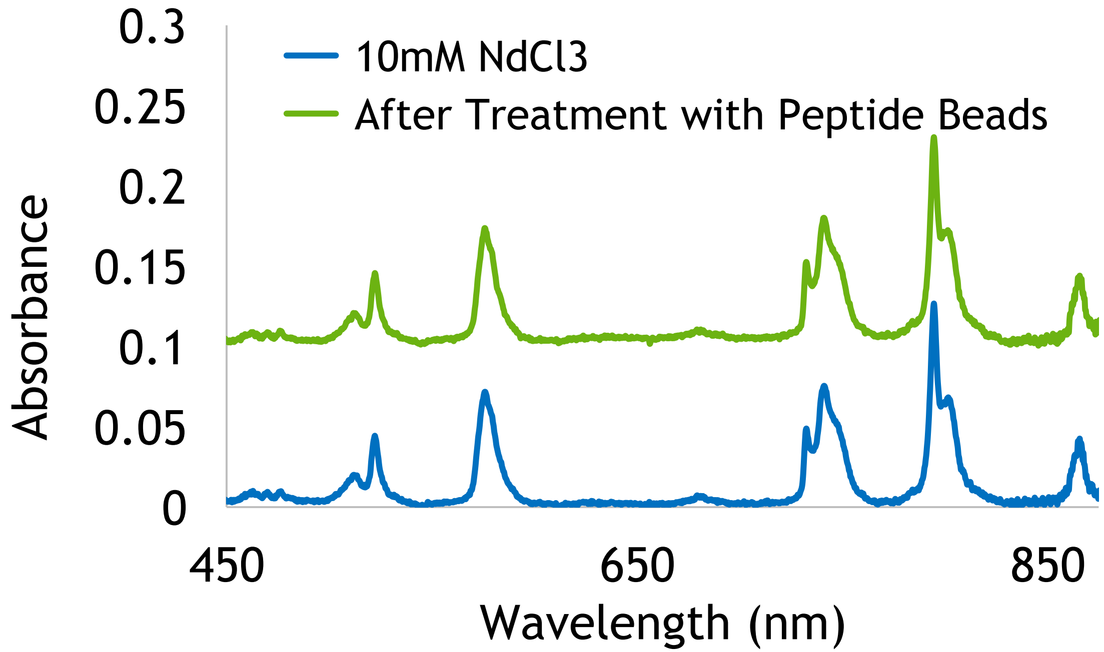
Exploring LanM Binding Sequence





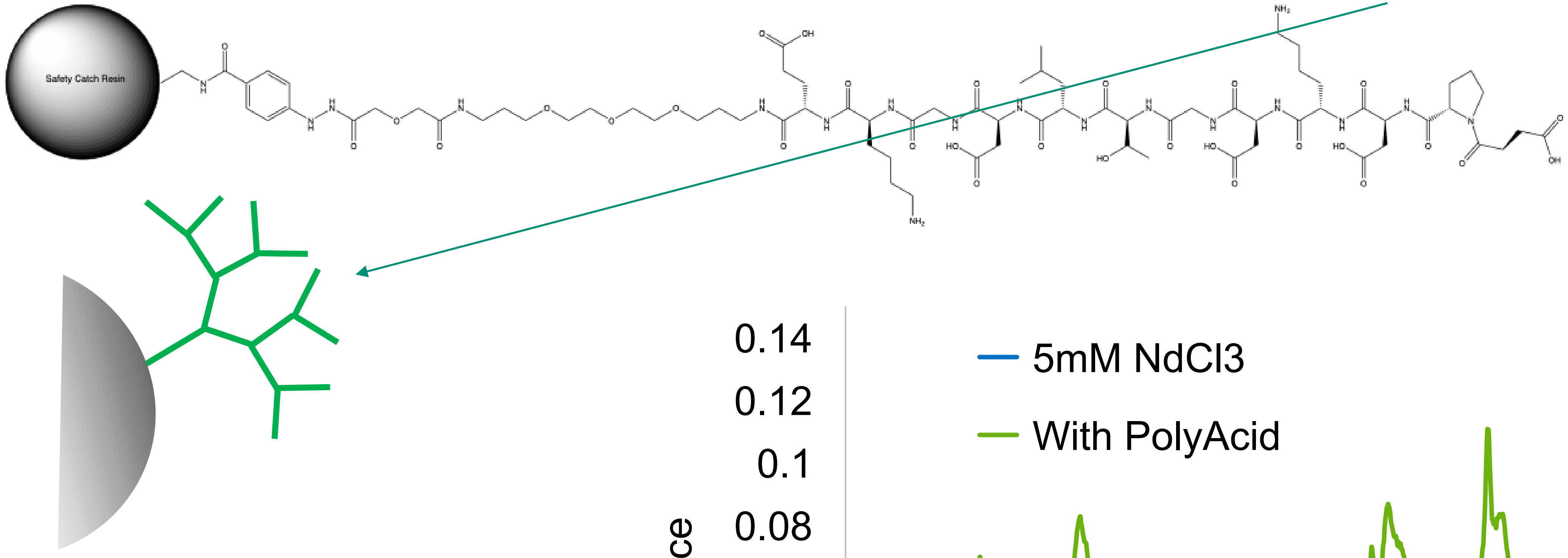
Cheisson, T. & Schelter, E. J. *Science* **363**, 489-493 (2019).

LanM binding consensus sequence:
D-P-D-(K/N)-D-G-T-(I/L)-D-x-(K/R)-E

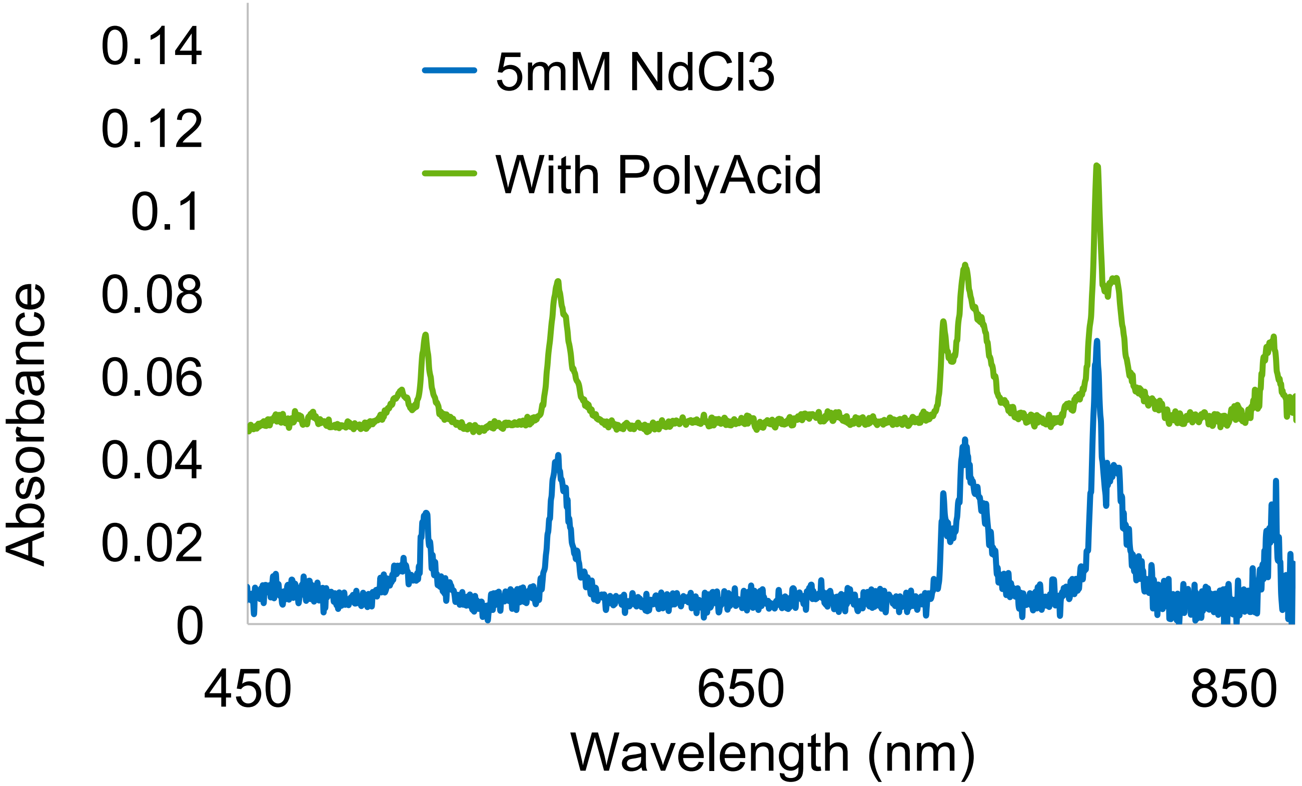


No binding detected…charge density? Peptide structure?

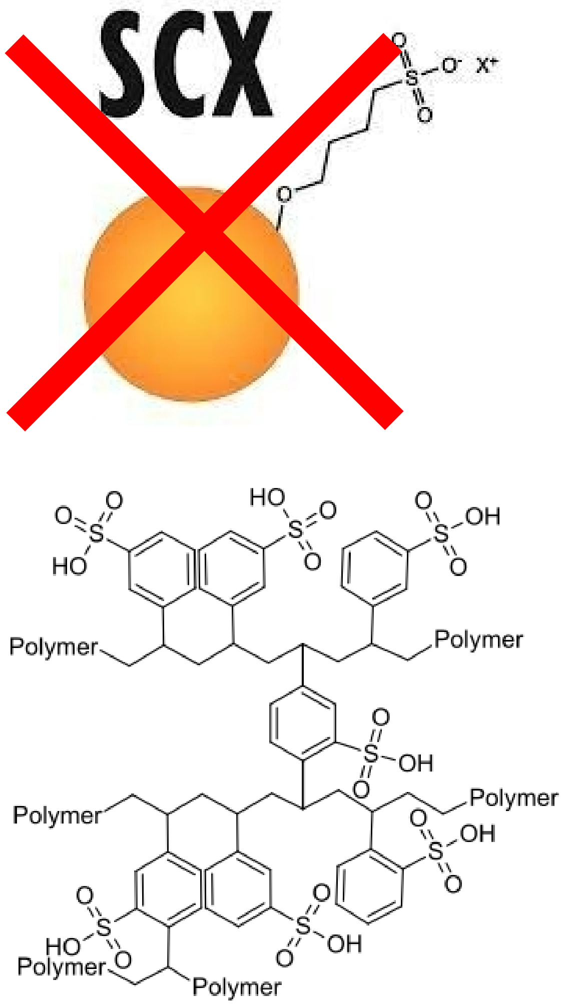
Simplifying Our Chemistry – Non-Specific Binding?



Decoration of beads with either carboxylates or phosphonates did not lead to removal of Nd^{3+} from solution!

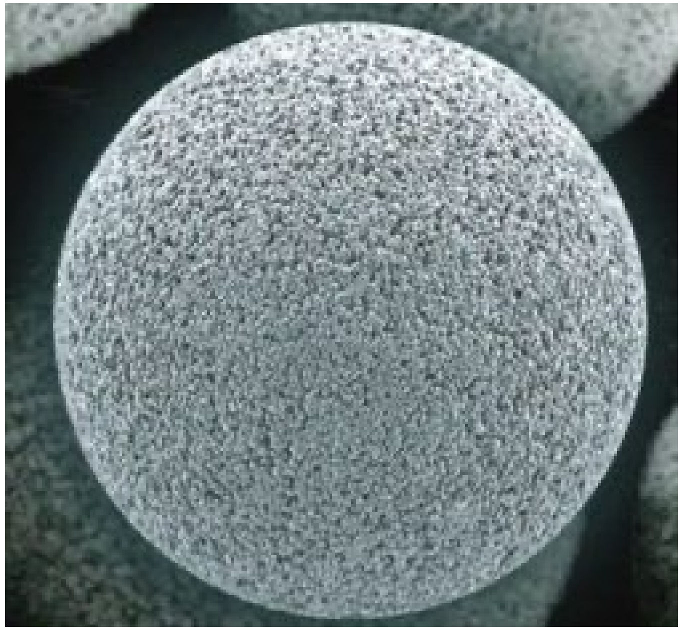


Composition Alone is Not Enough!



The structure of the solid support, as well as the structure of the peptide may be important!

Successful capture was enabled with a micro/nanoporous matrix…

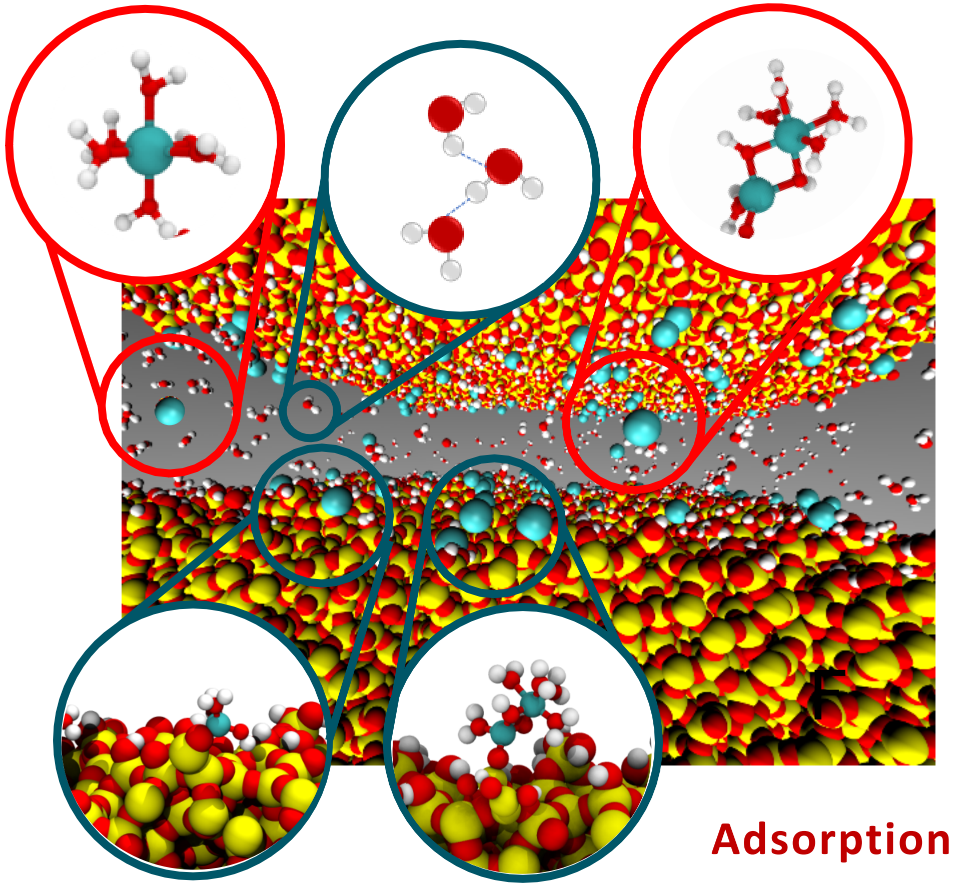


Commercial PSDVB-PA

Scale Bar

Nanoconfinement-Driven Capture of Lanthanides

| Anastasia Ilgen, Ph. D. | Geochemistry Department | Sandia National Laboratories | (505) 284 1393 | agilgen@sandia.gov |



Adsorption in nanopores

Can Ion Adsorption in Nanopores Enable Ion Selectivity?

Emergent chemical behaviors in nanopores:

- Decreased dielectric constant[1-2], surface tension[3], and density of water.[3]
- Decreased solvation energies of metal cations.[4]
- Increased inner sphere coordination of metal cations.[4]
- Enhanced metal adsorption[5-6], modified redox[7] and diffusion properties.[8,9]

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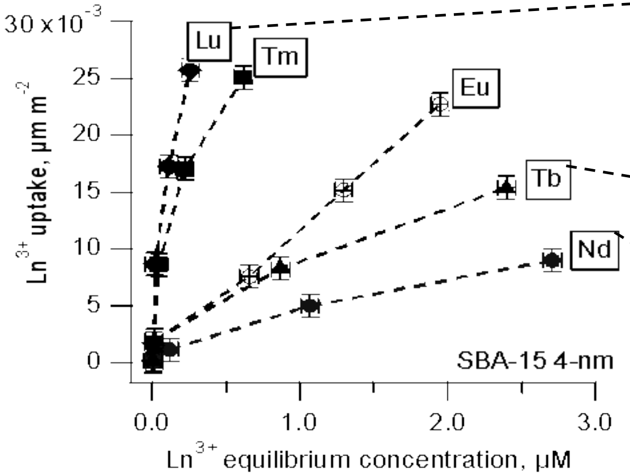
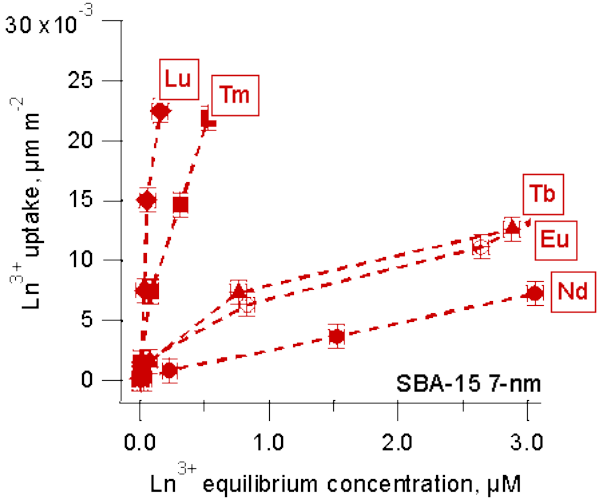
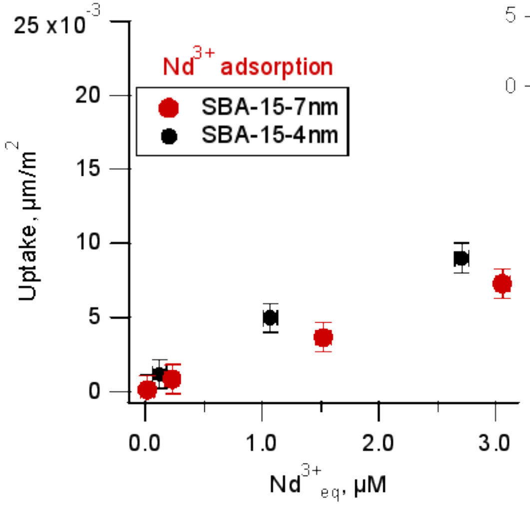
[1] Marti et al., *J. Phys. Chem. B* (2006)
[2] Senapati et al., *J. Phys. Chem. B* (2001)
[3] Takei et al., *Colliod Polym. Sci.* (2000)
[4] Kalluri et al., *J. Phys. Chem. C* (2011)
[5] Wang et al., *Geology* (2003)
[6] Zimmerman et al., *Environ. Sci. Techol.* (2004)
[7] Mattia and Calabro, *Microfliud Nanofluid* (2012)
[8] Samsom and Biggin, *Nature* (2001)
[9] Ma et al., *JACS* (2019)
[10] Chave et al., *Ultrasonics Sonochemistry* (2009)

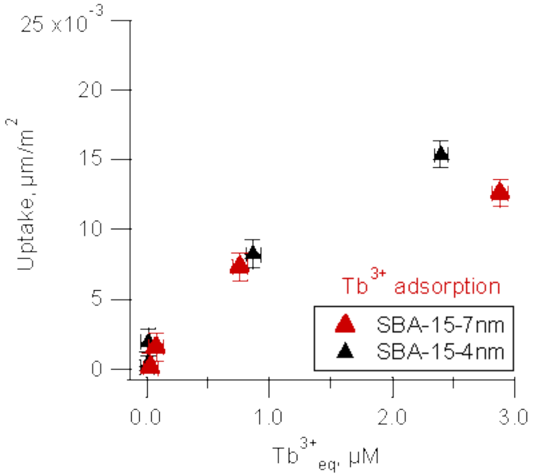
Ion Binding in Nanopores is NOT Uniform…

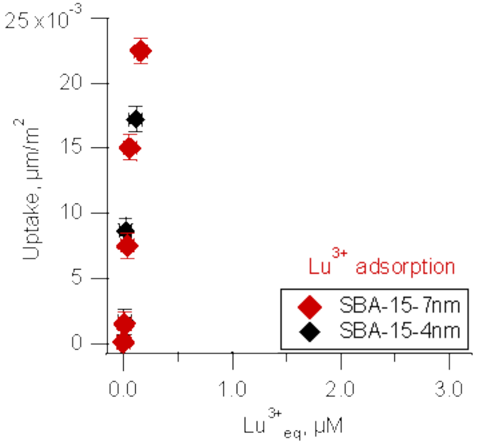
Mass-dependent uptake of <u>individual</u> Ln^{3+} ions onto porous SiO_2 with 4 nm and 7 nm pores.



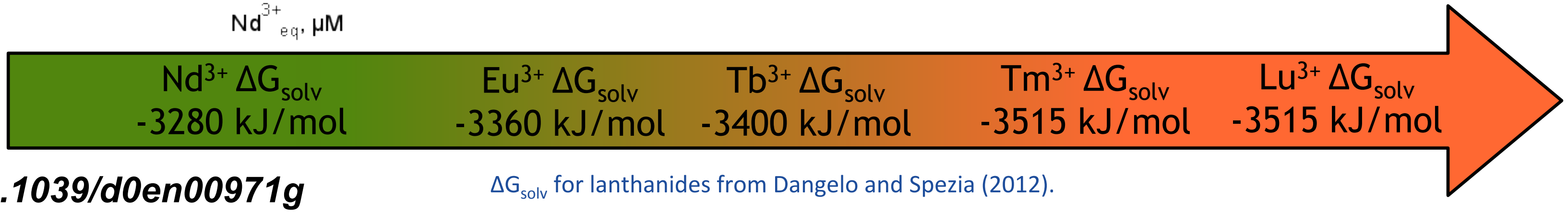








- **Pore-size-dependent adsorption is observed for weaker-hydrated lanthanides, while heavier lanthanide adsorption is independent of the pore size.**



Nd^{3+} ΔG_{solv}
-3280 kJ/mol

Eu^{3+} ΔG_{solv}
-3360 kJ/mol

Tb^{3+} ΔG_{solv}
-3400 kJ/mol

Tm^{3+} ΔG_{solv}
-3515 kJ/mol

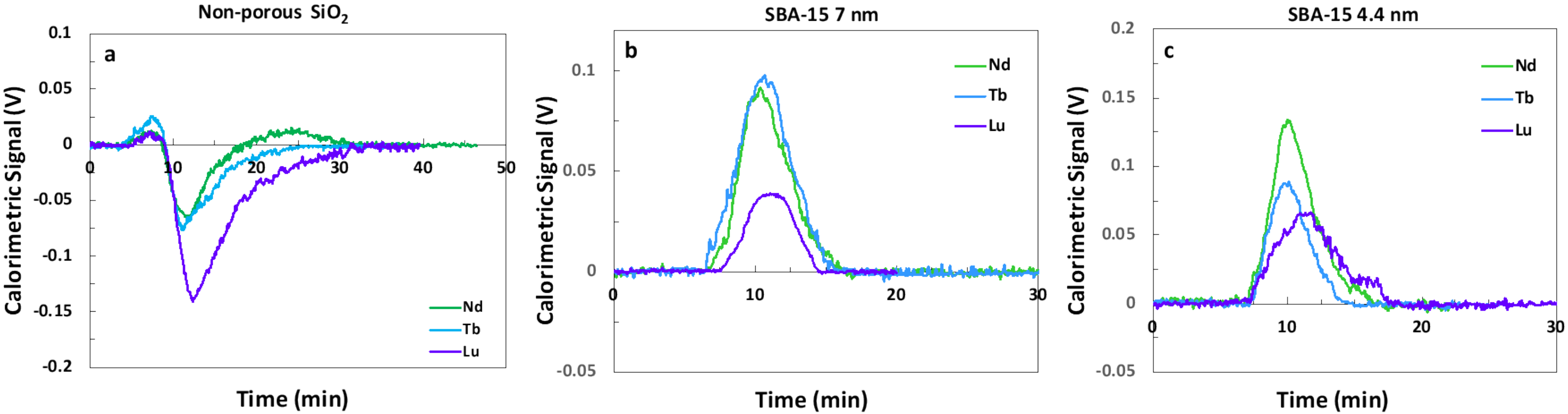
Lu^{3+} ΔG_{solv}
-3515 kJ/mol

Ilgen, et al., 2021. *Env. Sci. Nano* 8, 432. DOI: 10.1039/d0en00971g

ΔG_{solv} for lanthanides from Dangelo and Spezia (2012).

Nanoporous Ion Binding is *Different*!

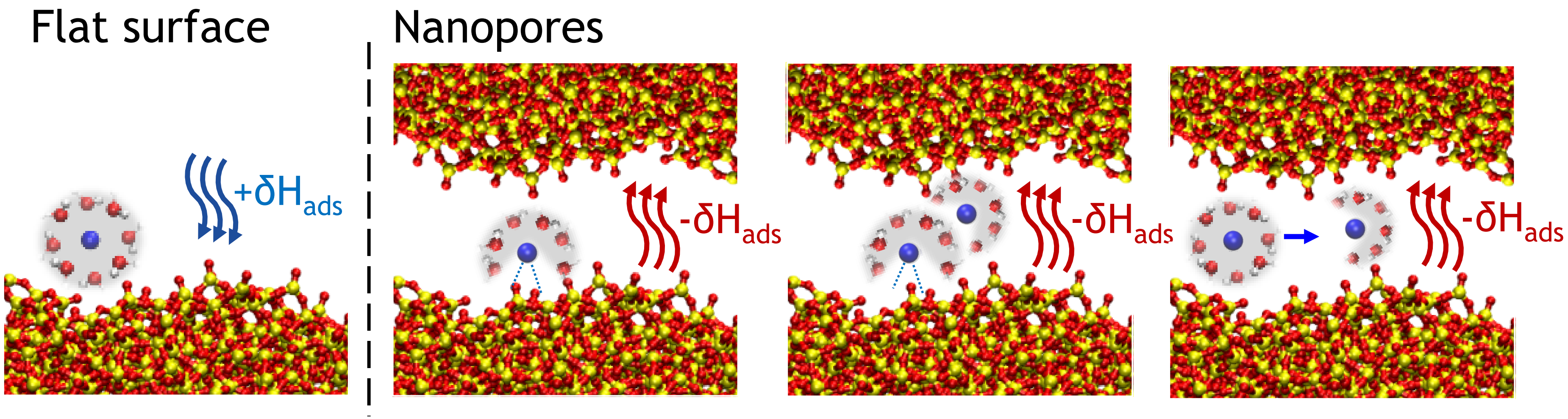
Total heats of adsorption for Nd^{3+}, Tb^{3+} and Lu^{3+} (a) for non-porous SiO_2; (b) for porous SiO_2 with 4.4 nm pores; and (c) for porous SiO_2 with 7.0 nm pores.



- Nd^{3+}, Tb^{3+}, and Lu^{3+} adsorption is exothermic on silica with 4-nm and 7-nm pores;
- Heat of adsorption depends on pore size;
- Adsorption is endothermic on non-porous silica.

Ilgen, et al., 2021. *Env. Sci. Nano 8, 432. DOI: 10.1039/d0en009*

Explaining Changes in Nanoporous Ion Binding



Three chemical mechanisms explain our observations:

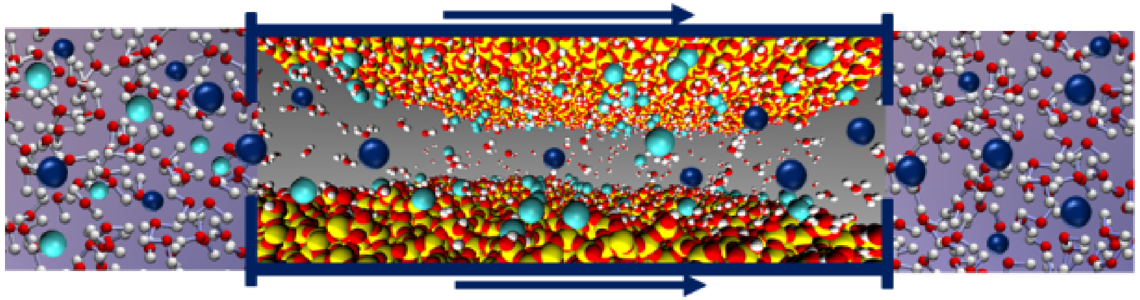
- nanoconfinement affects Ln^{3+} ΔG_{hydr}, impacting the energy required to achieve a dehydration reaction and the formation of an inner-sphere surface complex;
- nanoconfinement promotes inner-sphere complexation between Ln^{3+} ions and the SiO_2 or Al_2O_3 surface;
- nanoconfinement promotes the formation of polymeric Ln^{3+} species only on the surfaces of porous SiO_2 solids (not on non-porous SiO_2);

These cumulatively result in a dramatic shift in the energetics of Ln^{3+} adsorption, causing the reaction to switch from an *endo-* to an *exothermic* process.

An ion's ΔG_{hydr} determines whether (and to what degree) nanoconfinement will change its adsorption energetics and coordination environment on SiO_2 surfaces.

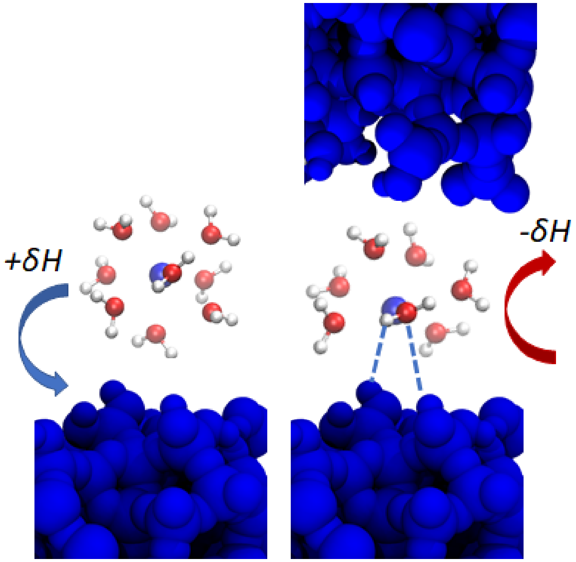
Ilgen, et al., 2021. *Env. Sci. Nano* 8, *432 DOI: 10.1039/d0en009*

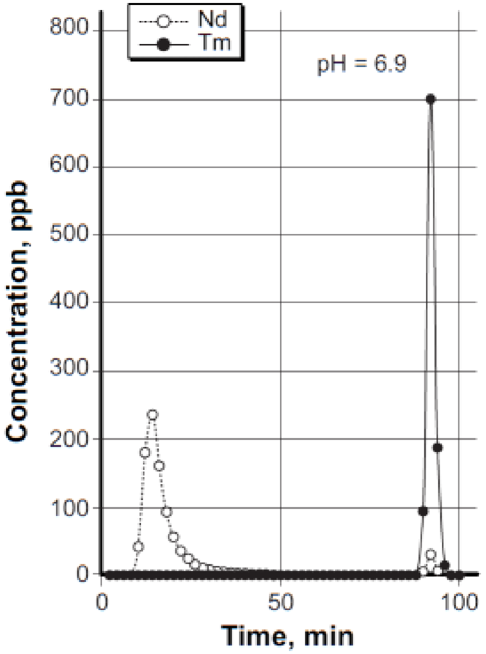
Realizing Selective Ion Binding in Nanopores



Separation Science

Understanding how Ln^{3+} adsorption structure and energetics change under confinement, enables improved separation strategies for critical rare earth elements.





Patent:

Ilgen, Non-provisional patent application “Systems and Methods for Separating Rare Earth Elements Using Mesoporous Materials”. Filed on 3/11/2020.

Transforming Coal-based Resources to Produce Critical Minerals

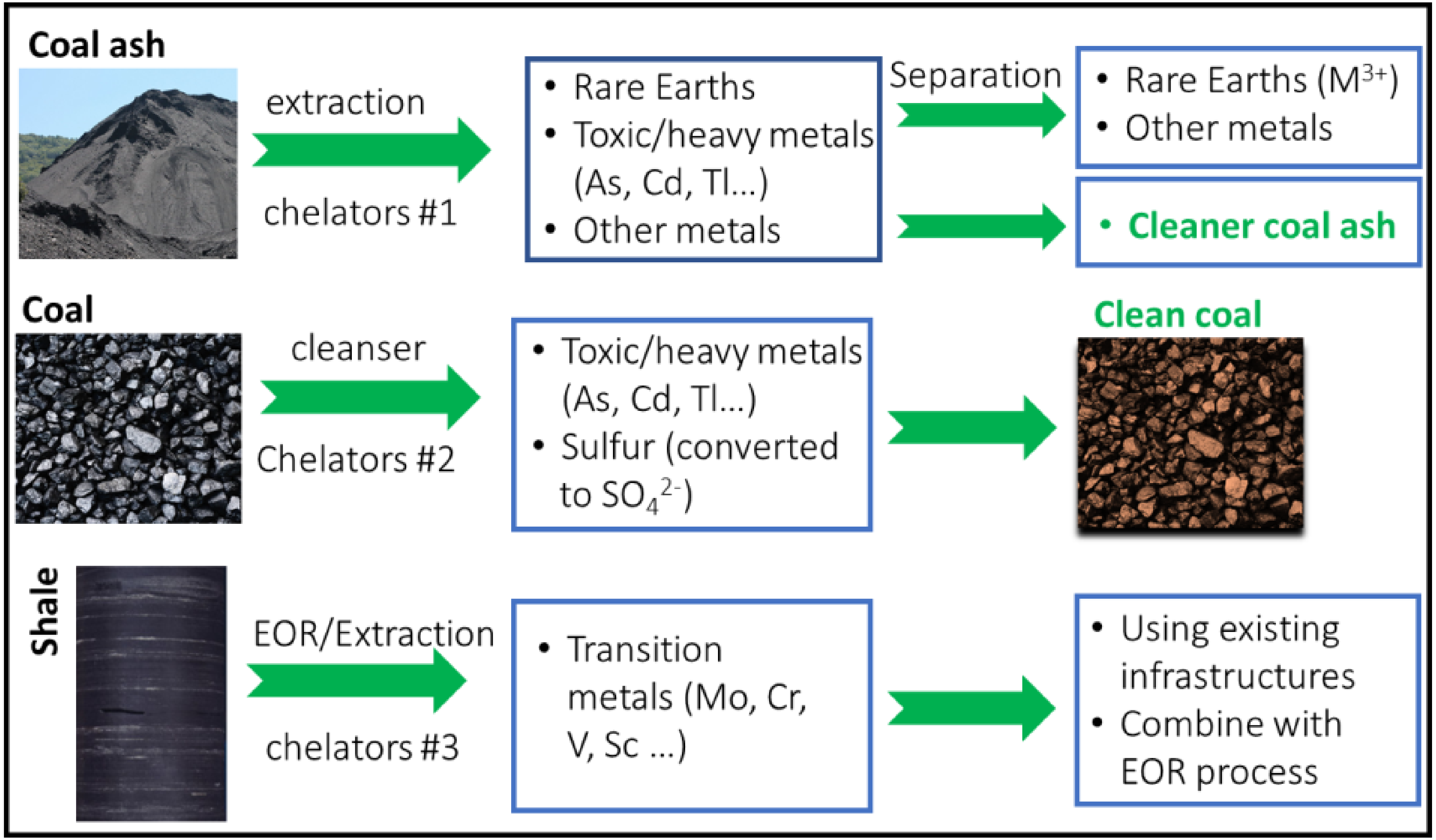
| Guangping Xu, Ph. D. | Geochemistry Department | Sandia National Laboratories | gxu@sandia.gov|

Recover critical metals and toxic metals from domestic resources (coal/coal byproduct/shale)

1. **Critical mineral sustainability requirement**
   - U.S. has vast natural resources of coal and shale, enough for hundreds of years of use.
   - Many coal seam, coal ash and shale intervals have REE contents that are more enriched than 20-40% conventional ore deposits
2. **Environmental sustainability requirement**
   - 3 billion tons of existing coal ash "polluting and causing damage" to the environment, additional tens of million tons generated annually
   - Coal ash is hazardous but not regulated as such, and EPA is proposing to regulate coal ash
   - Current extracting technologies using strong acids/bases, converting solid wastes into more hazardous solution waste
3. **Transforming vast natural resources of coal and shale to nonfuel Carbon-Based Products (CBP)**
   - Important to remove toxic metals in order for coal to repurpose CBPs

Sourcing Rare Earths Domestically

Three main domestic resources to recover critical metals and toxic metals



Coal ash

extraction

chelators #1

- Rare Earths
- Toxic/heavy metals (As, Cd, Tl…)
- Other metals

Separation

- Rare Earths (M^{3+})
- Other metals

- **Cleaner coal ash**

Coal

cleanser

Chelators #2

- Toxic/heavy metals (As, Cd, Tl…)
- Sulfur (converted to SO_4^{2-})

Clean coal

Shale

EOR/Extraction

chelators #3

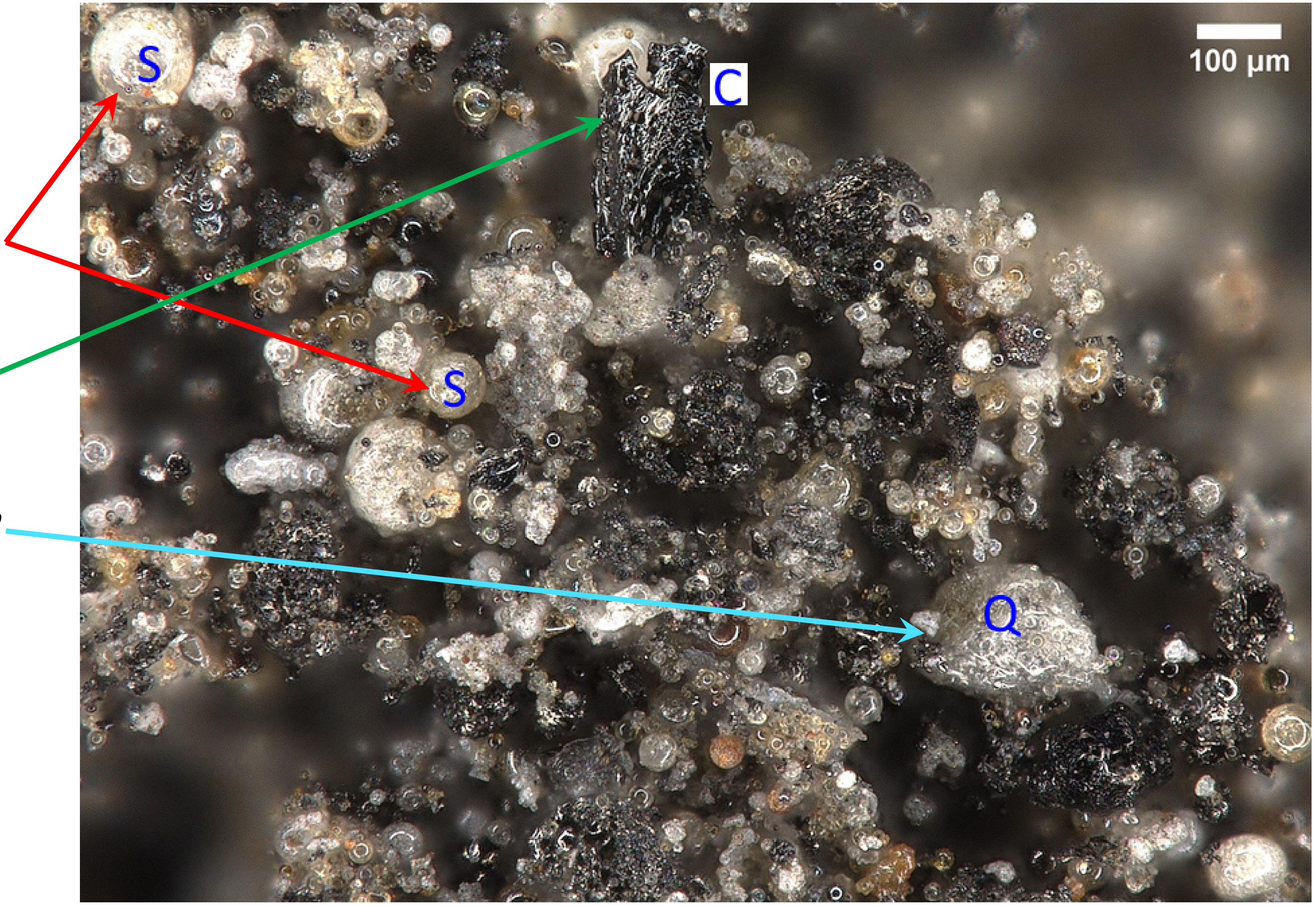
- Transition metals (Mo, Cr, V, Sc …)

- Using existing infrastructures
- Combine with EOR process

Guangping Xu

Finding Critical Materials in Coal Ash

Thera are several critical metal hosting phases in coal ash:



Amorphous silicate glass sphere (**S**)

Residual carbon (**C**)

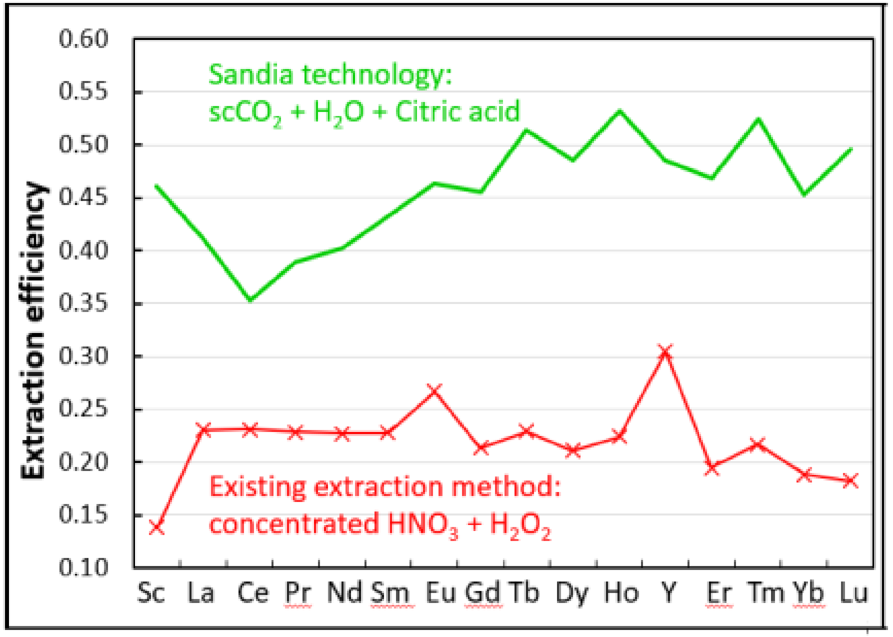
Accessory minerals (monazite, xenotime, quartz (**Q**) etc.)

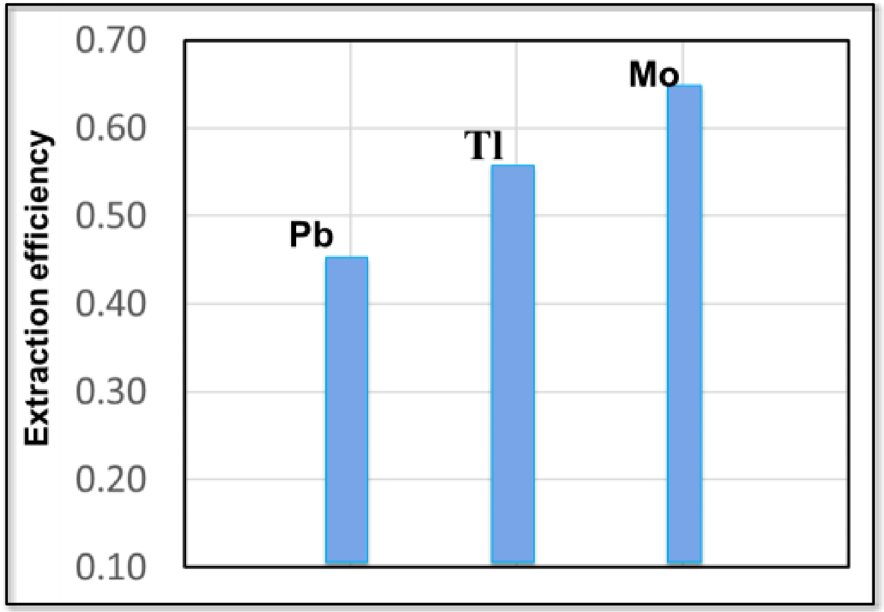
- ~40% entrenched inside glass sphere;
- ~60% critical metals are hosted in other phases.

Guangping Xu

Research Approach: $scCO_2$ + chelator + H_2O system

1. Supercritical CO_2 ($scCO_2$) is an excellent solvent.
2. Citric acid is an acid and also an excellent chelating agent.





- More than 50% heavy rare earths extracted without using strong acids/base
- 45 – 65% toxic/heavy metals were also removed, resulting in cleaner coal / coal ash for reuse

2021 R&D 100 Award: Gold Medal (1st Place) Special Recognition for Green Tech

Guangping Xu

Take Home Messages

- There is an important need to develop domestic sourcing of Rare Earth materials.
- Biological systems are powerful inspiration for sustainable, selective Rare Earth harvesting.
- Analogs to biological materials, however, must account for chemistry, structure, and environment.
- Ion confinement and highly efficient solvation and chelation offer promising potential for emerging Rare Earth harvesting technology.
- Future work that integrates biomolecular chemistry, controlled molecular environments, and engineered selective chelation may lead to new reliable, robust, domestic Rare Earth sourcing technologies!

Thank You!

Bio-Inspired Harvesting of Rare Earth Metals

Erik Spoerke*
George Bachand
Stephen Percival
Amanda Peretti
Susan Rempe
Krista Hilmas

Pengyu Ren (UT Austin)
Justin Gourary (UT Austin)

Nanoconfinement-driven capture of lanthanides

Anastasia Ilgen*
Kevin Leung
Louise Criscenti

Nadine Kabengi
(Georgia State U.)

Environmentally Benign Extraction of Rare Earth Metals

Guangping Xu*
Yongliang Xiong
Yifeng Wang
Mark Rigali

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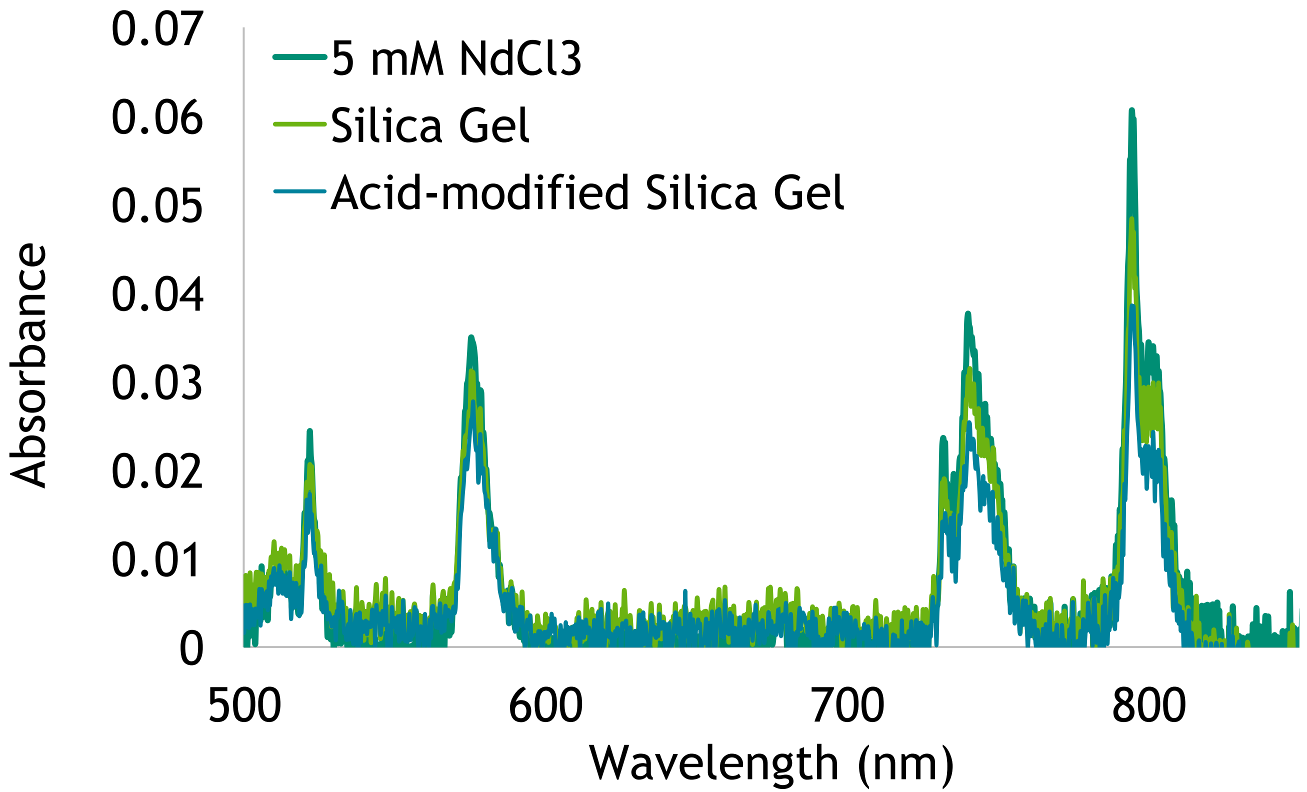
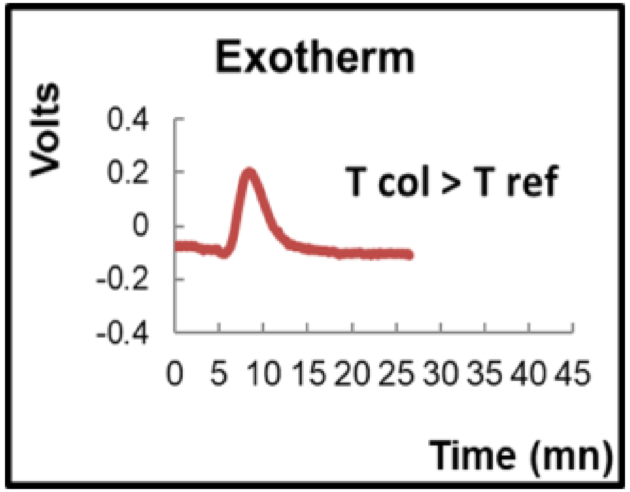
2. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.
2. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

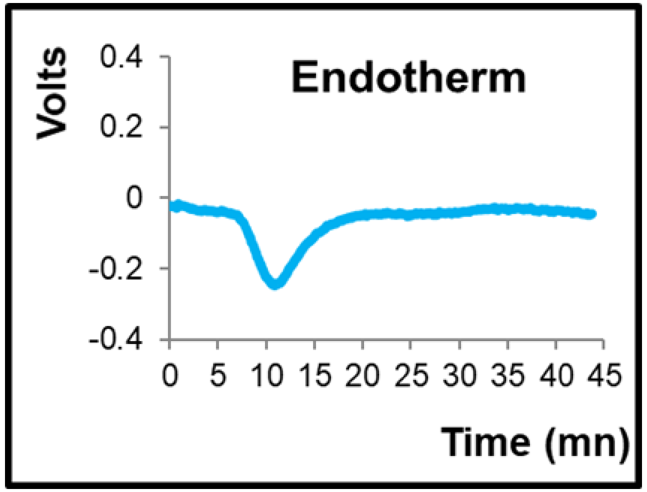
Backup Figures

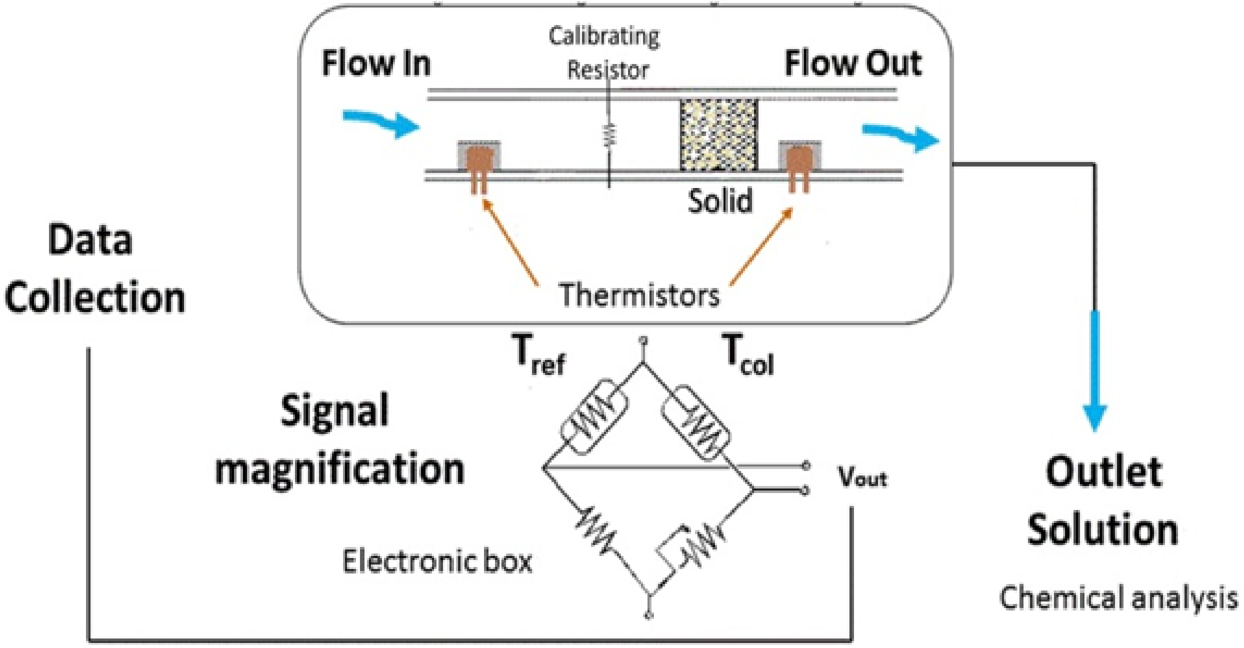
Acid-Modified Silica Gel



Quantifying Adsorption Energetics with Microcalorimetry





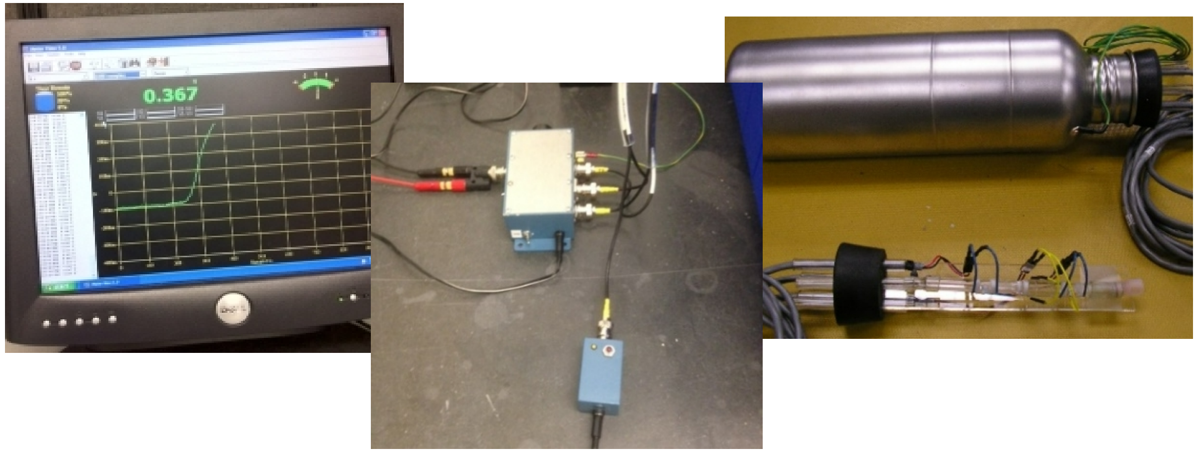


Data Collection

Signal magnification

Outlet Solution

Chemical analysis

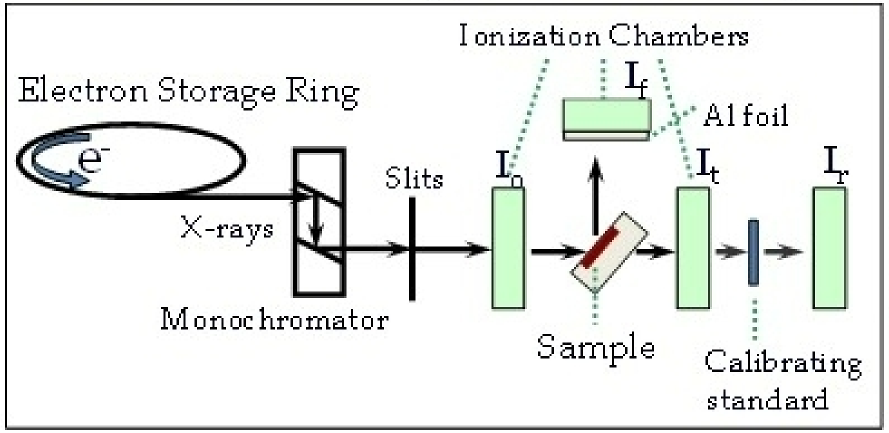


***In situ* experimental thermodynamics data at environmentally relevant P and T conditions**

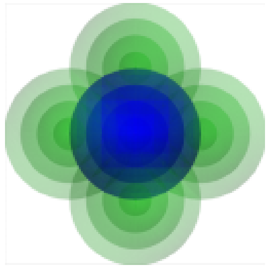
Assessing Adsorption Structures

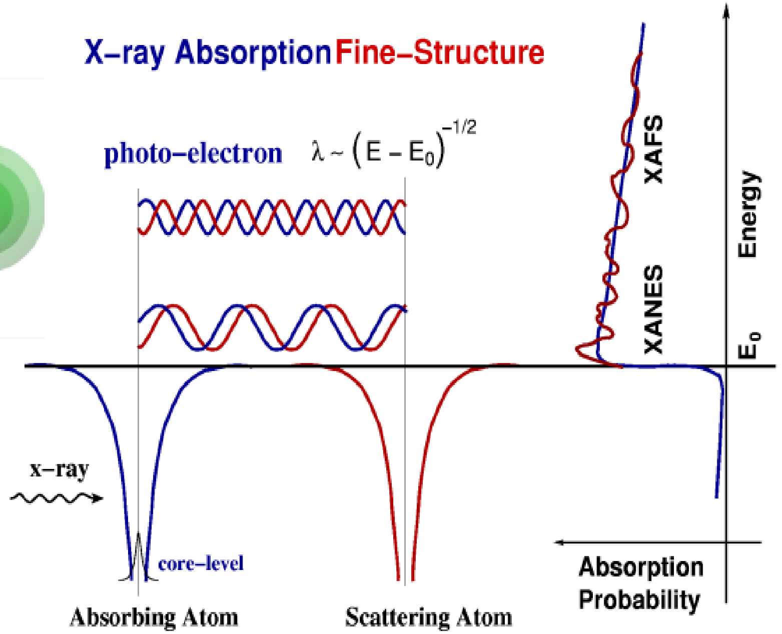
X-ray Absorption Fine Structure Spectroscopy (XAFS)

EXAFS spectroscopy instrumental setup

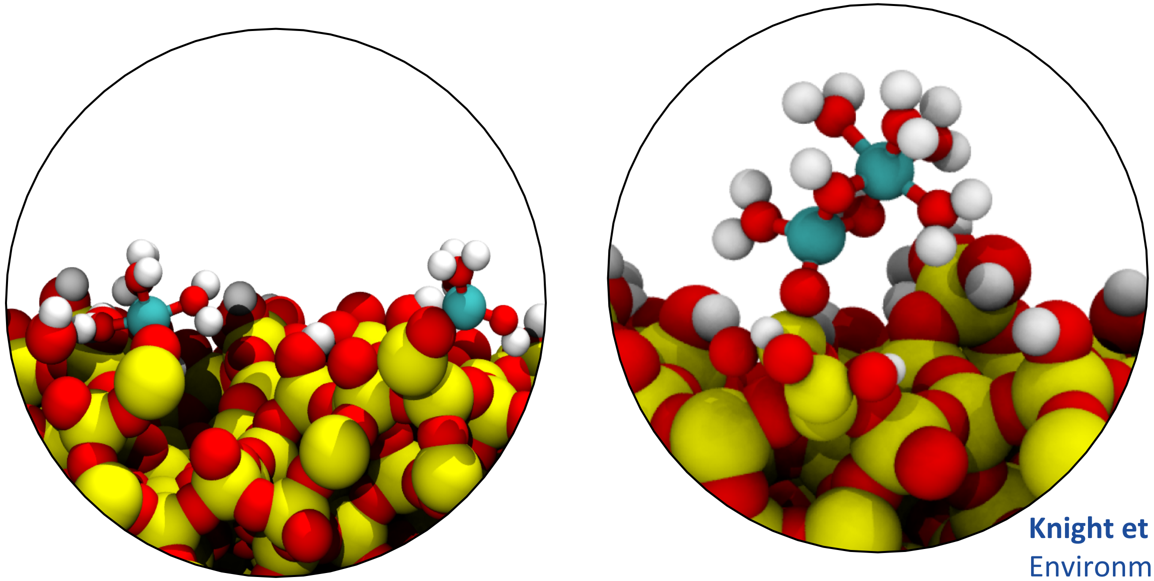


APS, Argonne National Lab.





XAS tutorial, xafs.org



Knight et al., Environmental Science Nano, 2020