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Strategies for Diversifying the Supply of Critical Materials for Clean Energy

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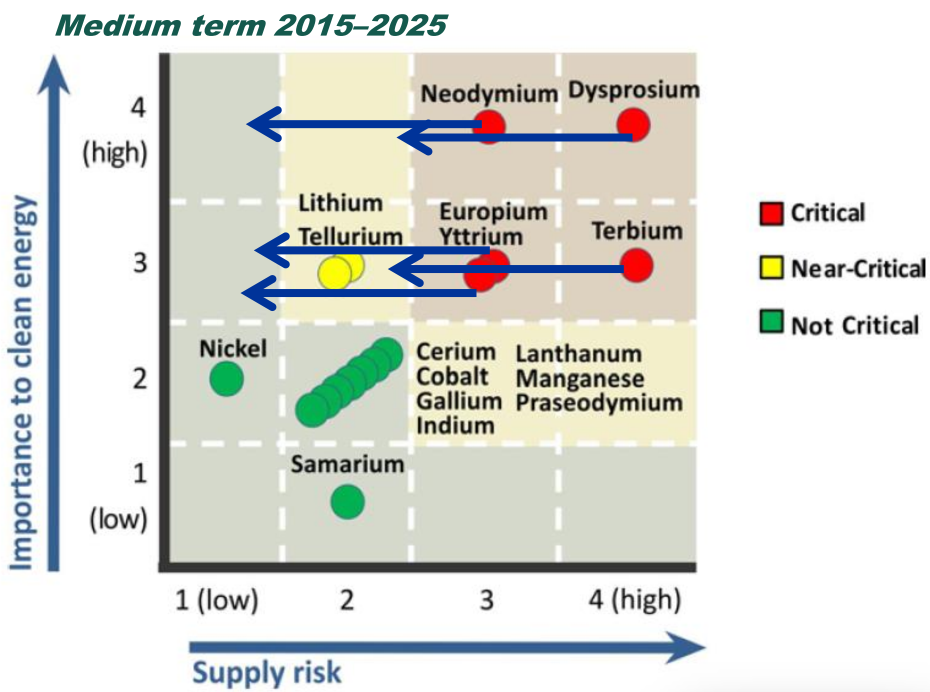
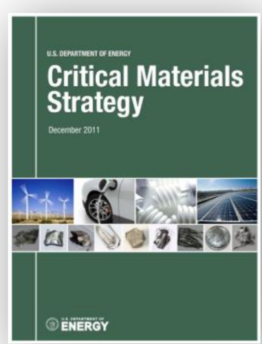
Oak Ridge National Laboratory, Oak Ridge, TN USA

248th American Chemical Society National Meeting, San Francisco, August 10–14, 2014

The Diversifying Supply Focus Area aims to reduce supply risk for critical materials



Taken from Figure ES-2 of the 2011 DOE Critical Materials Strategy document



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Target metals:

Critical: Nd, Eu, Tb, Dy, Y
Near critical: Li ~~and maybe Te~~
Abundant: La and especially Ce

Objectives:

- Provide new minerals-processing technologies that expand sources of critical materials.
- Increase the efficiency of separations and metals production processes, resulting in adoption of new technology by domestic industry.
- Develop significant new uses for co-products La and Ce large enough to have impact on TREO demand.

Four minerals account for most RE production

Increasing HREE content ↓

- Bastnaesite, $(La,Ce)CO_3F$
  - Most common RE mineral mined, mostly in China
  - Rich in LREE, lean in critical RE Eu, Tb, Dy, and Y

- Monazite, $(La,Ce,Pr,Nd,Th,Y)PO_4$
  - Found widely in placer deposits
  - Minor processing in India and Brazil
  - Significant radioactivity raises costs

- Xenotime, YPO_4
  - Good source of HREE
  - Minor processing in Malaysia
  - Also radioactive

- Ion adsorption clays
  - Rich source of HREE, but limited in supply
  - Mined in southern China, much of it illicitly and with pollution

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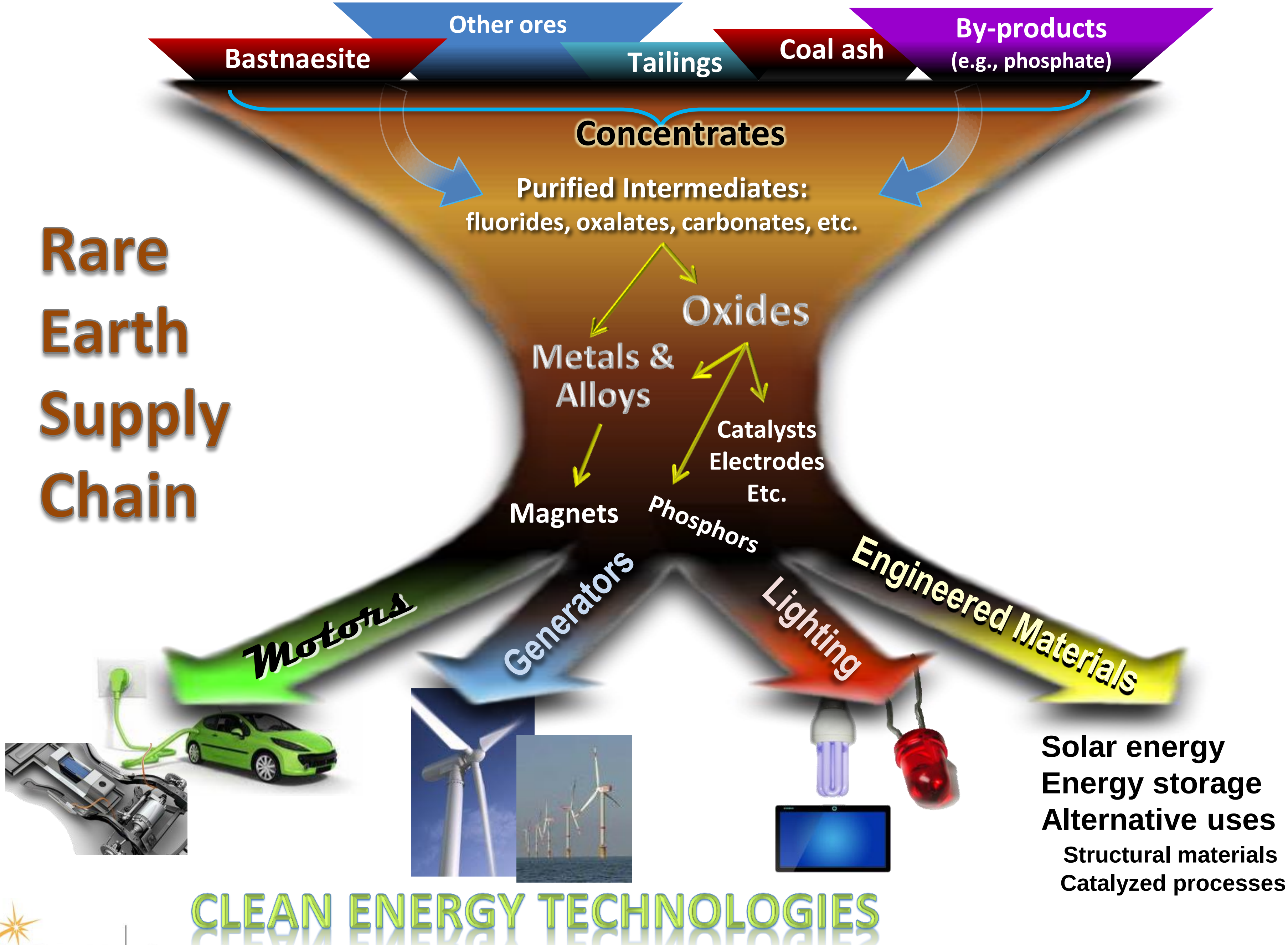
Images thanks to Wikipedia

Rare Earth Supply Chain



Potential RE resources are vast and dispersed, but only a few operating mines account for the bulk of world supply

Kaiser Research Rare Earth Resource Centre

iNEMI White Paper: Rare Earth Metals, 2014

Why do we need to diversify the supply of CMs?

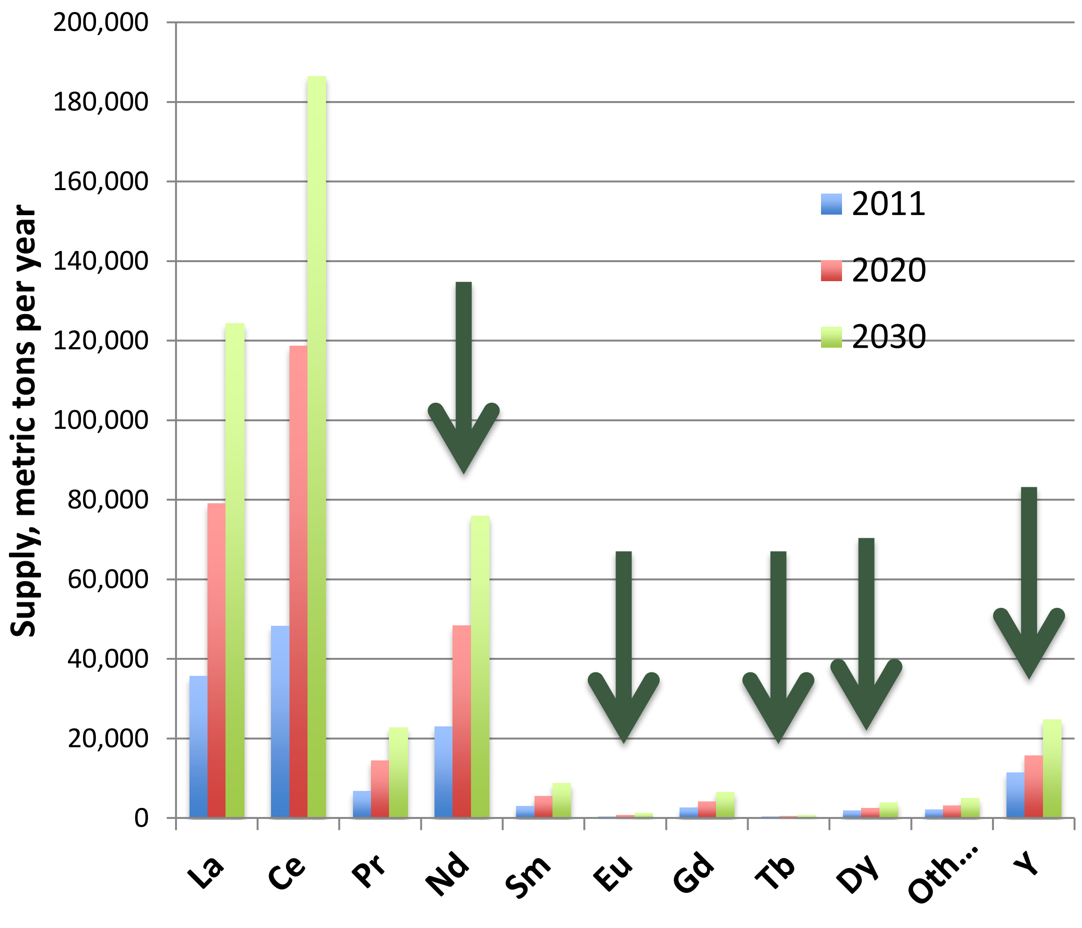
- **Demand for REs and Li projected to grow**
- **~90% of REs come from a single country (China)**
- **We currently rely mostly on a single RE mineral**
  - **Bastnaesite excellent source of LREE**
  - **But bastnaesite is lean in four critical REs Eu, Tb, Dy, and Y**
- **Numerous sources are underutilized**
  - **Recovery of REs from Molycorp ore is only 65%**
  - **Wasted REs in phosphate rock ≈ world production of RE**
  - **Tailings and coal ash are a potentially vast supply**
  - **Radioactivity in some ores (e.g., monazite) inhibits access**
- **Separations and conversion to metal mostly in China**
- **Little recycling of RE is performed**
- **Substitution is a daunting challenge**

"Thorium problem" impedes supply of REs

- Dilemma: Ores rich in desired HREE tend to be high in Th content, frustrating access to such ores
- Radioactive materials add cost to processing due to regulations related to health and environment
- Thorium has almost no market, so any recovered Th becomes a waste that is expensive to dispose of
- Hopes for a Th nuclear fuel cycle creating a large new market for Th in the future are ill-founded
- Therefore there is no revenue to offset the added cost
- Technical solution is to avoid concentrating Th or embrace optimism and find new applications for Th
- Regulatory solution could be government Th stockpile

Supply of REE is non-uniform

- Supply projected to grow rapidly
- Dominated by LRE, especially La and Ce
- Relatively lean supply of critical REEs Eu, Tb, Dy, and Y



Ray Moss, et al., EUR 25994 EN, 2013

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Supply projected to meet demand for TREO, but HREO projected in short supply with Ce in excess

	Demand	Supply
Ce	60,000–70,000	75,000–80,000
Nd	25,000–30,000	30,000–35,000
Eu	625–725	450–550
Tb	450–550	300–400
Dy	1,500–1,800	1,300–1,600
Y	12,000–14,000	9,000–11,000
Tot REO	150,000–170,000	180,000–210,000

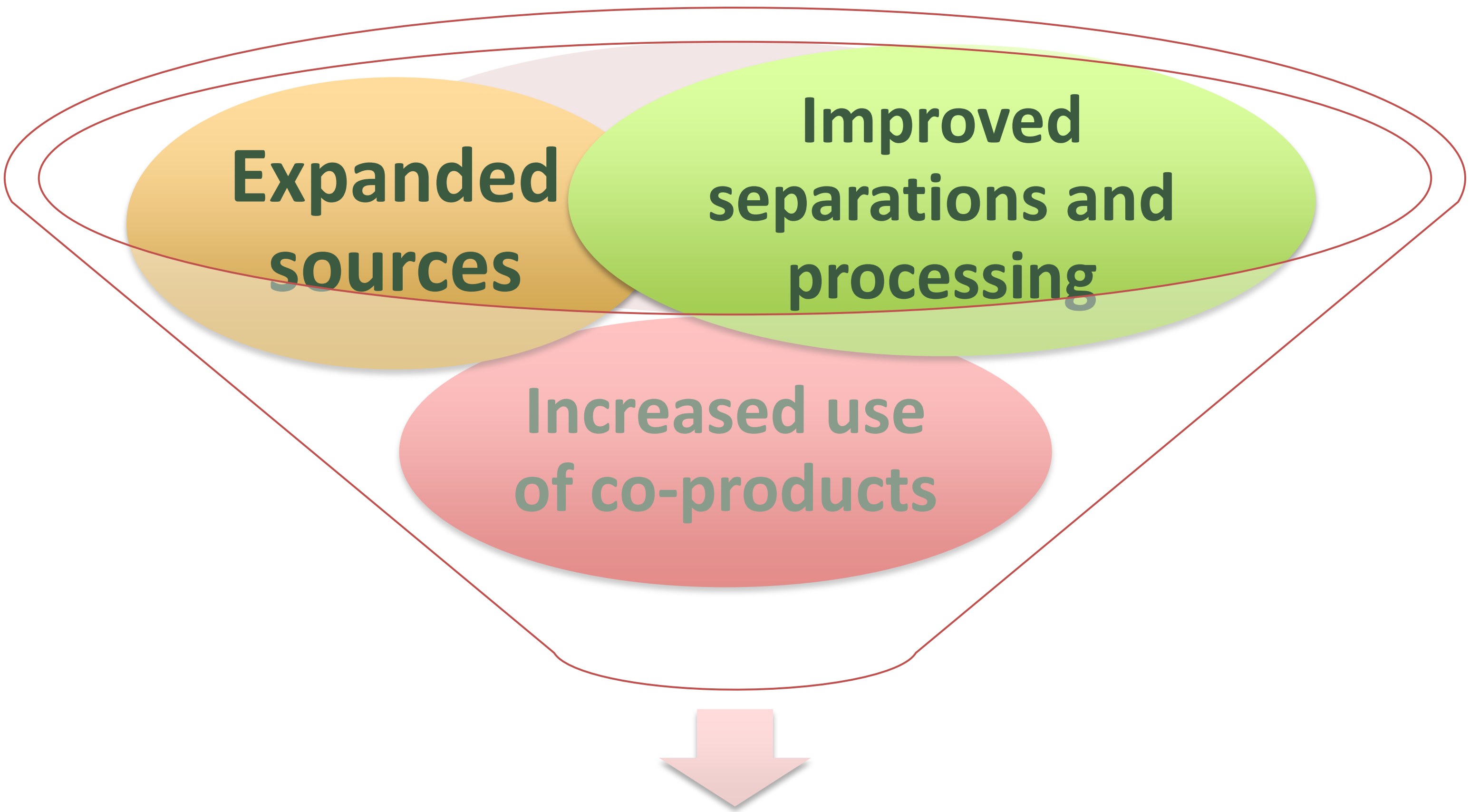
Projections for 2016 in tpa REO.

Source: D. J. Kingsnorth, "Rare Earths Supply Security: Dream or Possibility," Strategische Rohstoffe-Risikovorsorge, Freiberg, April 2012.

What are the technology gaps in the RE supply chain?

- Complex and costly extraction technologies—most developed for bastnaesite
- Low mineral selectivity in beneficiation
- Low extn selectivity from ores concentrates
- Poor economics of extraction from lean sources
- Inefficient separation of adjacent lanthanides
- Costly and polluting conversion of oxides to metals
- Limited applications for co-products (Ce, La, Th)

A THREE-PRONGED STRATEGY IS BEING PURSUED



DIVERSIFIED SUPPLY

Eight projects in three thrusts address gaps

New Sources

- Advanced beneficiation techniques (CSM, ORNL, Molycorp, Cytec)
- Recovery of REEs and U from phosphate (ORNL, INL, Cytec, FIPR)
- Recovery of Lithium (Simbol, ORNL)

Transformational Separations

- Adjacent lanthanide separations (INL, ORNL, Molycorp, Cytec)
- Conversion of metal oxide to metal, alloys, and materials (CSM, ORNL, Ames, Cytec, Molycorp)
- Ionic-liquid based separations processes (ORNL, Cytec)
- Computational prescreening of ligands (Ames, ORNL, Cytec)

New Uses

- New lanthanide-based catalysts (Ames, ORNL, Dow)

Lithium recovery project aims to increase lithium supply to meet growing demand

Simbol, ORNL

Geothermal reserves of Li can supply new demand, expected to triple by 2025

Improved separation agents for recovery of of LiCl from Salton Sea geothermal brine
- **High-capacity sorbent materials**
- **High-throughput membranes**

Improved methods for concentration of LiCl
Improved membranes for converting LiCl to LiOH

Simbol facilities in Pleasanton, Brawley (demo plant at right), and Calipatria, CA

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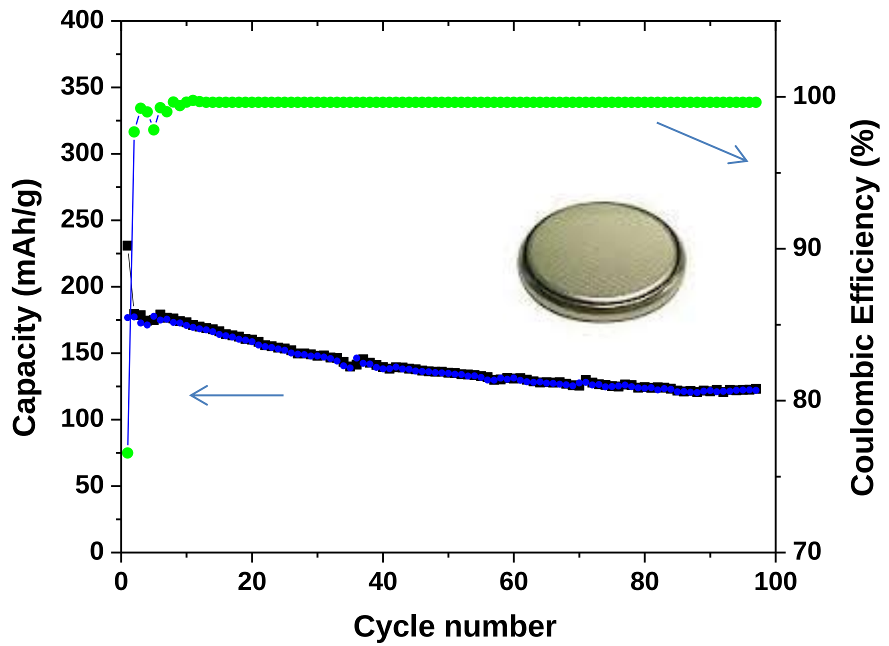
SIMBOL materials

Recent result: Li ion battery demonstrated for lithium salts obtained from geothermal brine

M. P. Paranthaman, J. Luo, Z. Bi (ORNL); S. Harrison (Simbol Materials)

- Cathodes prepared from Simbol's Li_2CO_3 obtained from geothermal brine.
- Important step towards electrical energy storage application made possible by extraction of lithium from geothermal brine.

- Research Details
  - Cathode materials prepared from both commercial and geothermal Li_2CO_3.
  - X-ray diffraction and SEM reveal similar crystal structure and microstructure.



Cycling performance of Lithium-ion battery: Half-cell configuration: $LiNi_{0.7}Co_{0.3}O_2$/ 1M $LiPF_6$ in EC/DEC electrolyte/ Li metal at c/10 rate

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Advanced beneficiation project aims to increase flotation selectivity and recovery

CSM, ORNL, Cytec, Molycorp

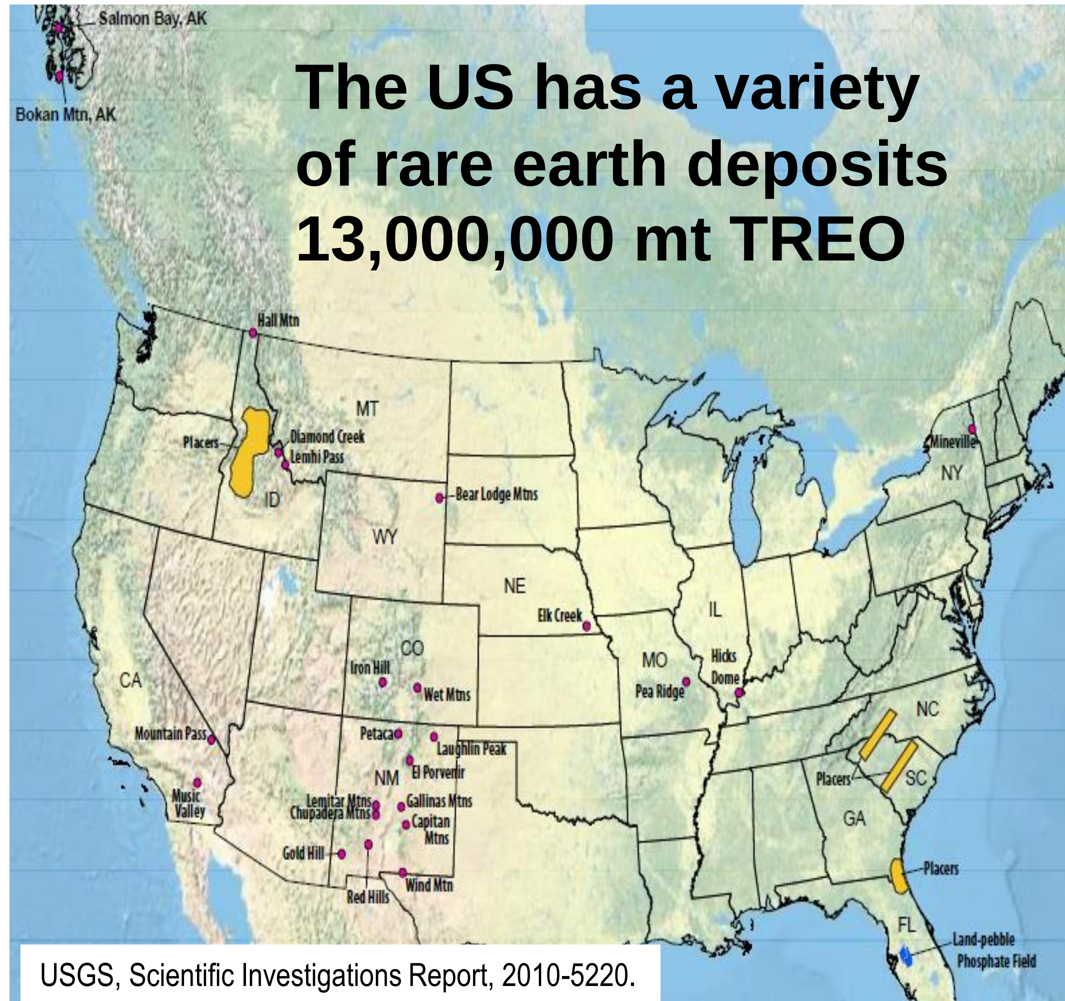
Beneficiation key to processing RE ores.

Froth flotation major technique and cheap, but is currently only working for bastnaesite.

But froth flotation recovers only 65% of the RE at Mountain Pass.

Improvement in selectivity will increase recovery as well as make additional ores accessible.

Project seeks major advance in froth flotation of REE minerals bastnaesite and monazite.



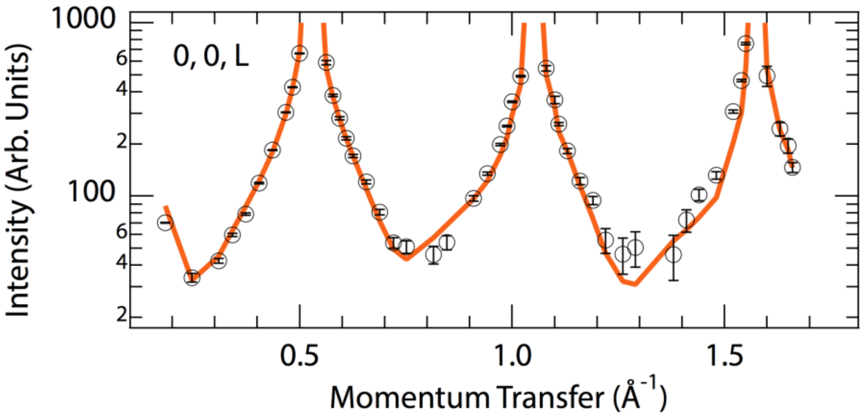
The US has a variety of rare earth deposits 13,000,000 mt TREO

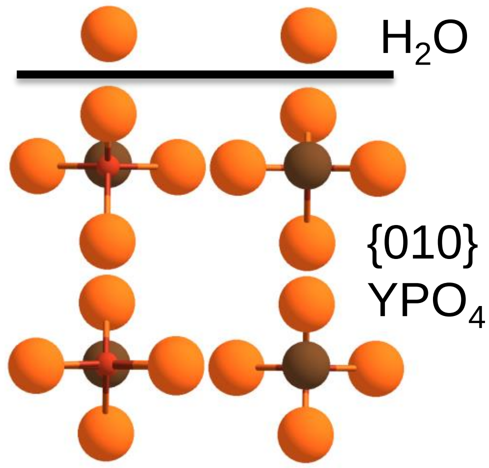
USGS, Scientific Investigations Report, 2010-5220.

Interface structure of HREE mineral xenotime (YPO_4) measured at the Advanced Photon Source

Result will help:

- Understand the effects of pretreatments on mineral structure.
- Determine efficacy of flotation agent adsorption.
- Rational design of highly selective flotation agents





Left: Data points and preliminary fit. **Right:** Surface structure from fit (oxygen, yttrium, phosphorus)

- Research **Details**
  - Beamline at APS, 2013.
  - Fitting reveals stoichiometric surface termination plus adsorbed water.
  - Measurements on other REE minerals synthesized by ORNL are planned.

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CSM, ORNL, Cytec, Molycorp

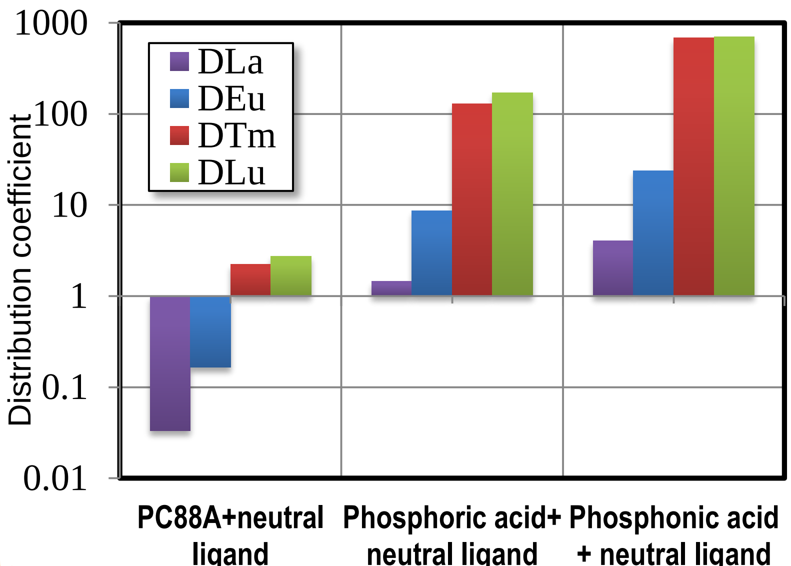
Recovery of REEs and U from Phosphate Ore Project taps potentially vast REE supply

ORNL, INL, Ames, FIPR, Cytec

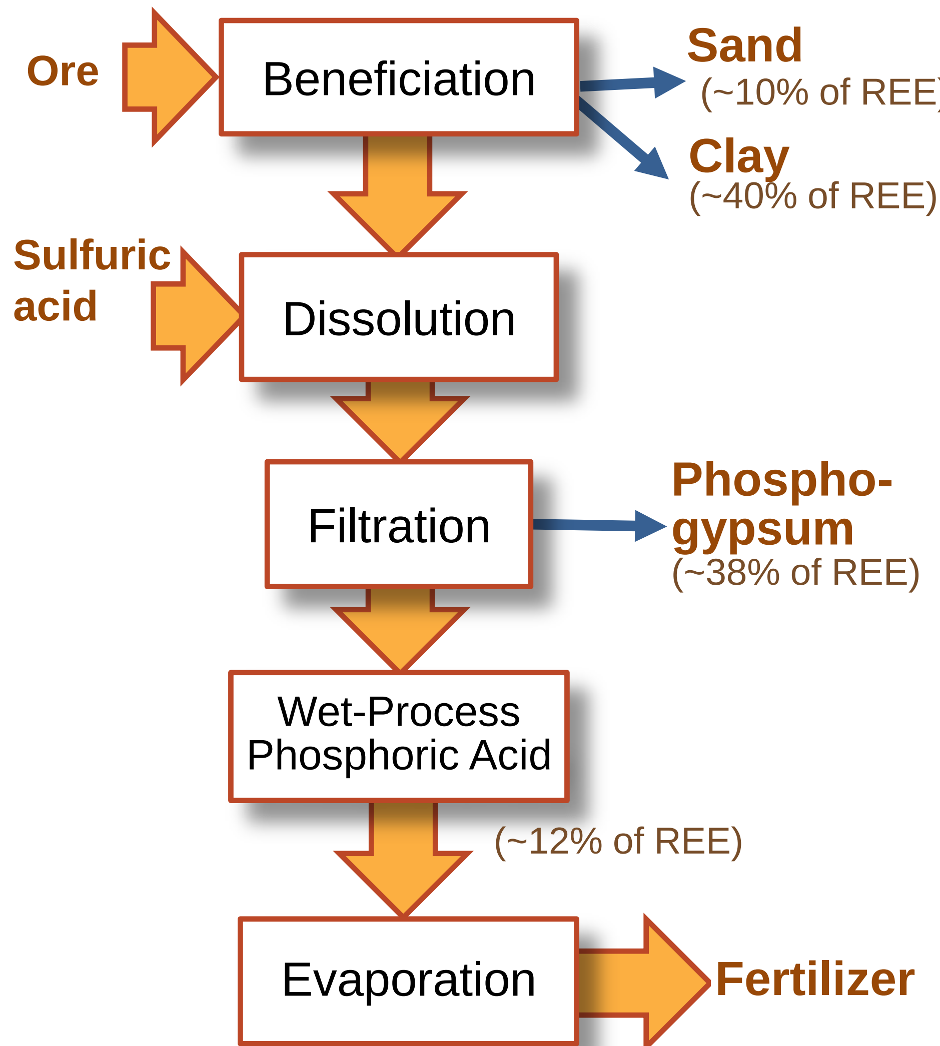
28,400,000 mt/y phosphate rock mined in US

REE	MT/y	% 2013 global supply
Y	3600	89%
Nd	2500	14%
Dy	380	56%
Eu	100	38%
Tb	40	26%

Result in 2014: Extraction of 4 lanthanides from industrial phosphoric acid sample from FIPR



Streams being examined:

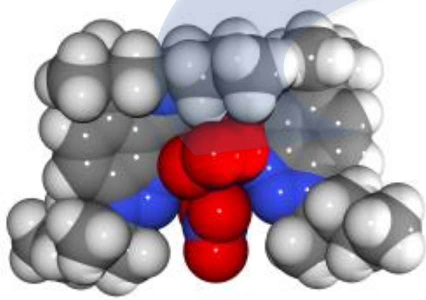


Higher separation factors needed for adjacent RE

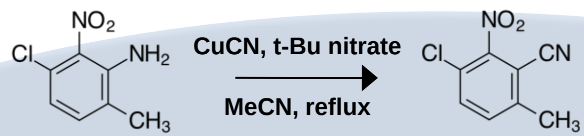
Challenge: Slight differences between the ionic radii of adjacent lanthanides make them extraordinarily hard to separate

Opportunity: Preorganized extractants could dramatically improve the economics of producing pure REE (esp. Nd, Tb, Dy, Y)

Design



Lanthanide complex with computationally designed extractant molecule



Synthesis

Testing

Commercialize d new extractants and processes

(INL, ORNL, Ames, Cytec, Molycorp)

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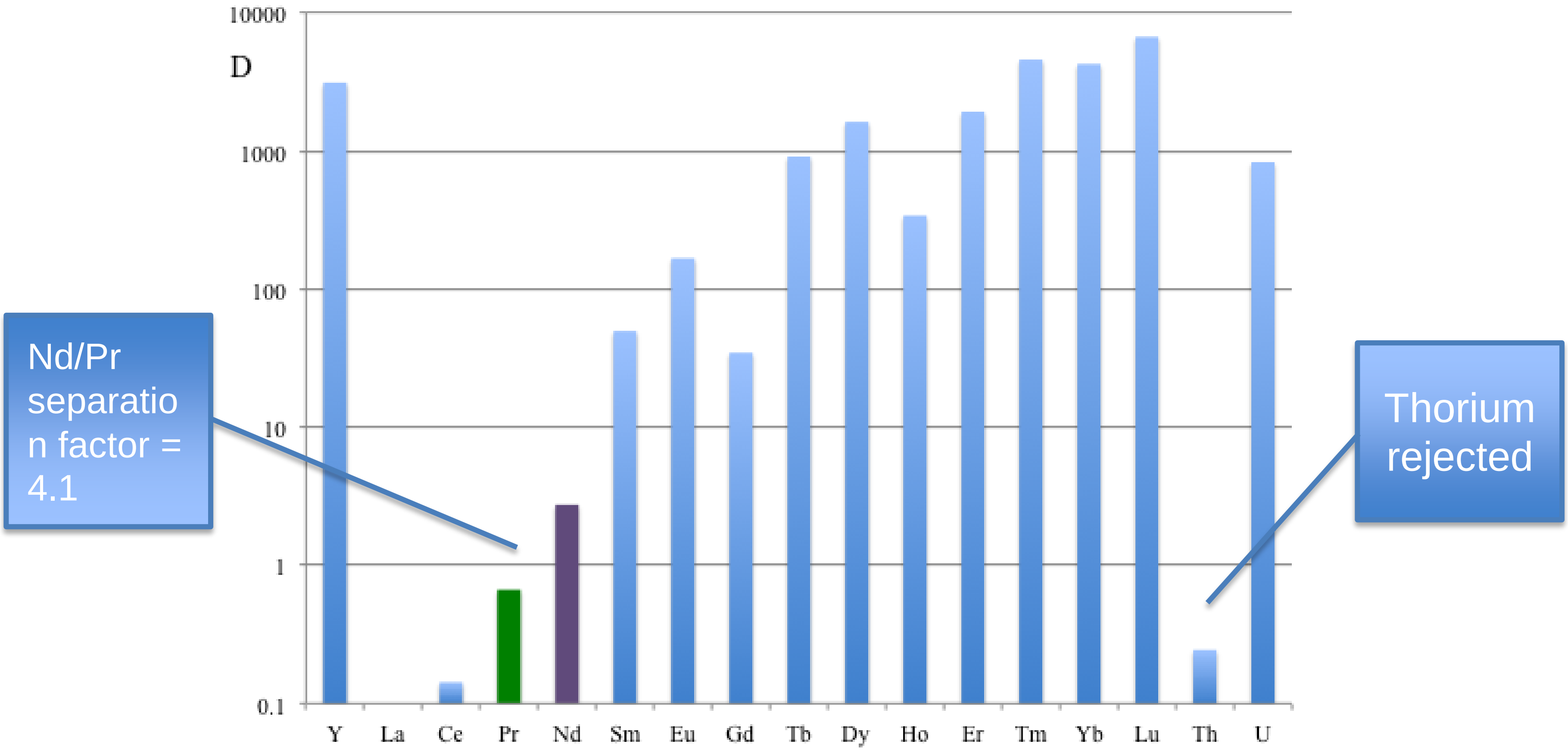
New extraction systems are delivering high intra-lanthanide separation factors



Extractant in dodecane. Metals at trace concentration in 5 M HCl. Process-relevant feeds being studied next.

SX mixer-settler test bed set up at INL

- 30 stages of mixer-settler units
- Total throughput (O+A) ~0.2 Lpm with high turndown ratios
- Components compatible with Cl, NO_3, PO_4, SO_4 media
- Rapid development and testing of flowsheets with new extractant systems
- Joint INL-Cytec tests under way

Project seeks improved technologies for conversion of RE oxide to metal

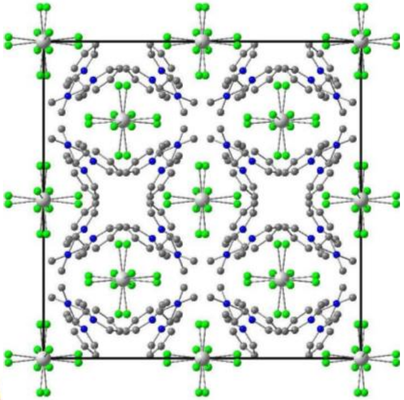
CSM, Ames, INL, Molycorp

Processing only being done in China, using inefficient and polluting methods

- First strategy is to develop carbohalogenation in molten salts

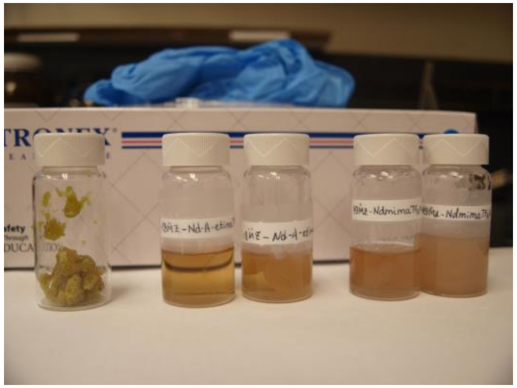
Current and past processes for REO to metal reviewed. Carbochlorination scheme verified through a lab-scale reactor & preliminary economic evaluation completed.

$$REO + C + Cl_2 \rightarrow ReCl_3 + CO_2$$



$(PyrrH)_3DyCl_6$

- Second strategy is to develop low-T route in ionic liquids



Nd ILs up to 1.2 M

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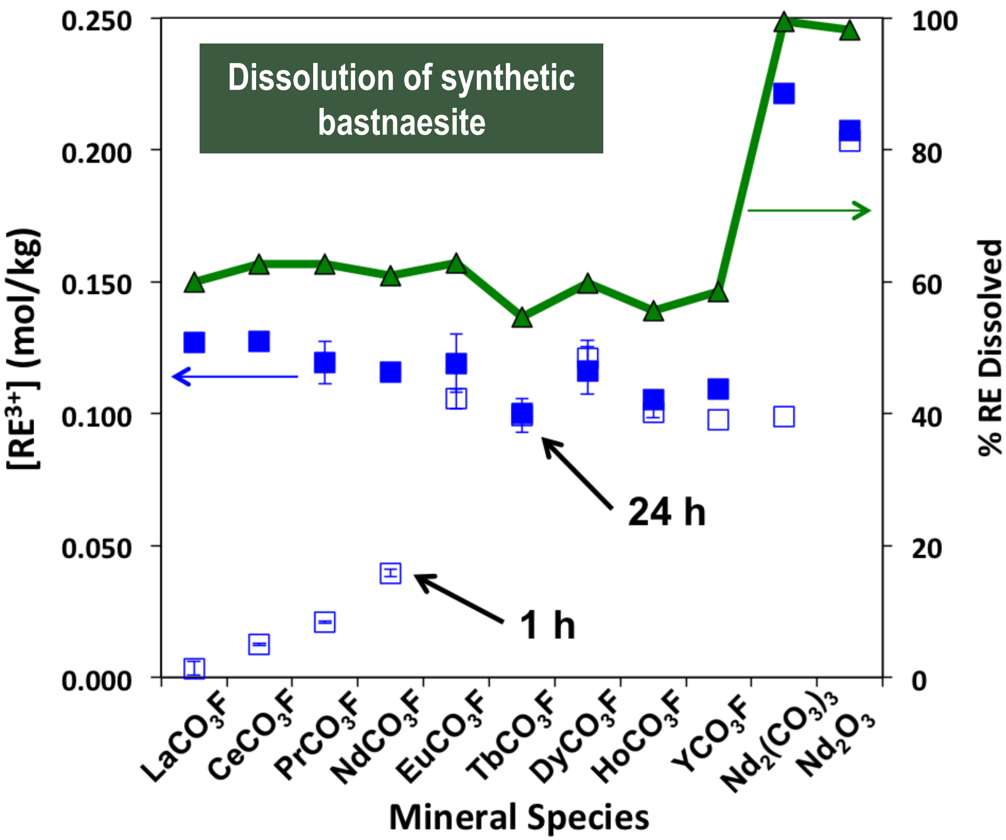
Ionic liquids dissolve RE minerals

- TSILs dissolve RE oxides and carbonates, including bastnaesite
- Enables separations and electrolysis of loaded TSILs
- Produces RE^{3+} ions plus REF_3 solids; kinetic discrimination

- Research Details
  - Effective dissolution of $RECO_3F$ at 120 °C by prototype IL system
  - Generality to other ILs and temperatures down to RT 25 °C
  - Journal article prepared
  - Invention disclosure submitted



ORNL, Ames, Cytec, Molycorp

Computer-aided molecular design (CAMD) process will speed time to solution

Molecular mechanics (MM)
- Fast but inaccurate w/o good parameters
- Parameterization is laborious and slow

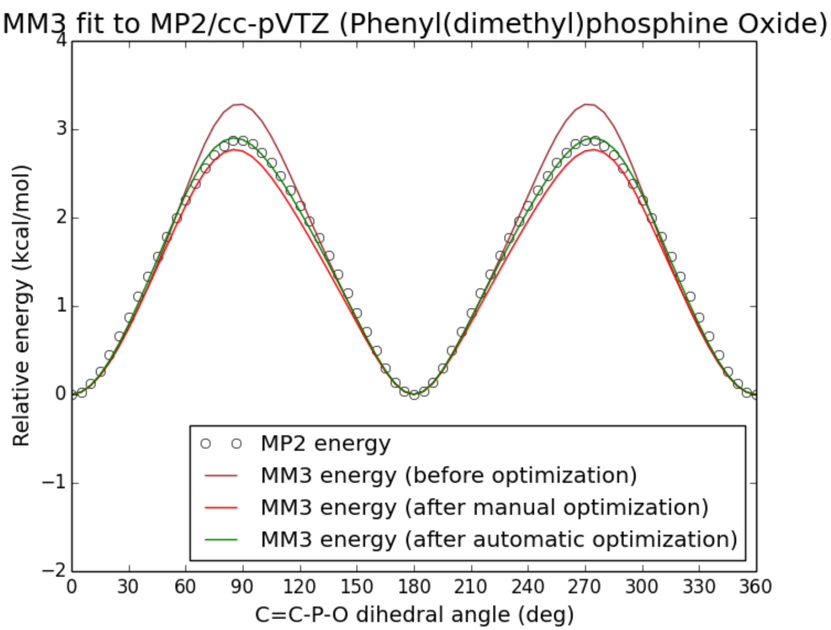
Quantum mechanics (QM)
- Accurate but slow, complex

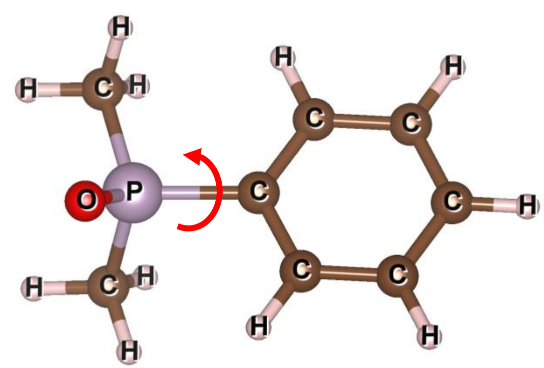
A prototype code to optimize MM parameterization developed using QM.

It will speed up the first step of ligand design, force-field parameterization.

Ultimately, we will be able to perform ligand design in months vs years.

Example of MM parameterization





Bond rotational energy

Ames, ORNL

Catalyst precursors synthesized for high-throughput catalyst screening

$$3\ KC(SiHMe_2)_3 + LnI_3THF_4 \xrightarrow{\text{benzene, 12 h}} Ln\{C(SiHMe_2)_3\}_3$$

Addressing Ce surpluses through high value applications

ν_{SiH} = 2107 and 1829 cm^{-1}

Yellow easily isolated crystals

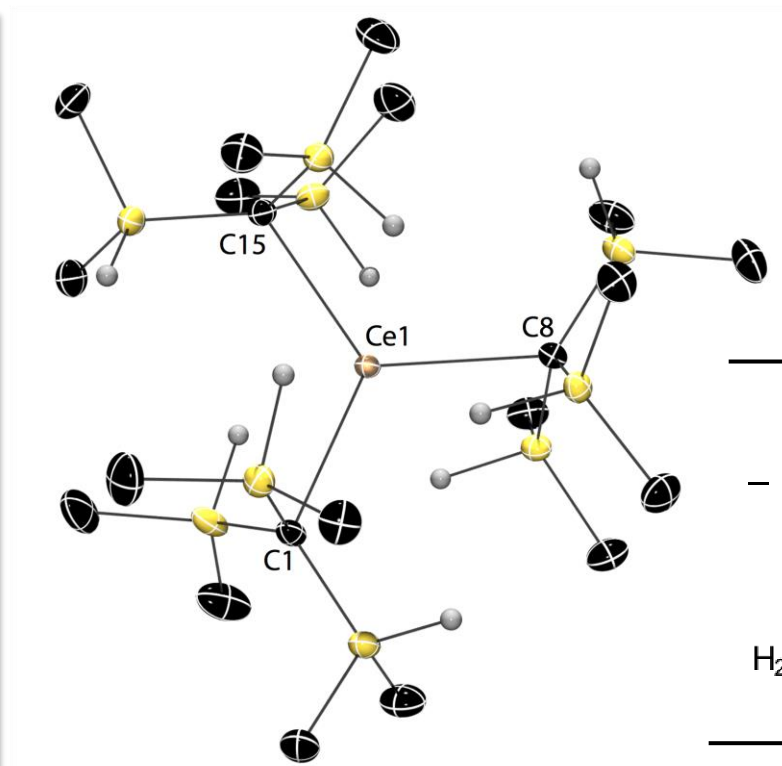
Gram-scale trisalkyl Ce(III), La(III), and Pr(III) organometallic complexes isolated.

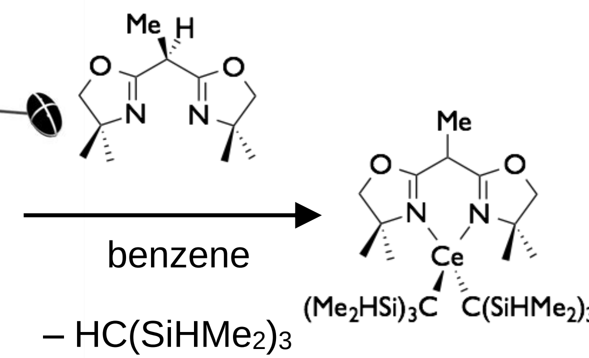
Thermally stable.

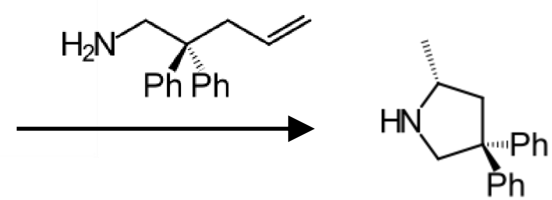
Precursors for new families of catalysts.

For hydroamination or polyethylene manufacturing.

Interacting with Dow.







hydroamination catalysis

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Broad R&D strategy for CM supply developed

- Supply of CMs currently risky, not well diversified
- Demand is growing but not well balanced vs supply
- Significant technology gaps exist in the supply chain
- Three-pronged strategy initiated; new sources, transformational processing, new uses of co-products
- User facilities engaged, theory/computations being used, equipment set up
- Six invention disclosures files and “percolating”
- Industry involved, commercialization pathways paved

Thanks to the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

And Thank You!

Questions?

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Rare Earth Distribution % | By Mineralization

	Mt. Pass Bastnaesite	China Byan Obo	HRE-China Laterite		Selected Monazite	Pea Ridge* Breccia	Pea Ridge** RE-Apatite	Florida Phosphate
Lanthanum	33.8	27.1	1.8	Light Lanthanides	21	27.5	18.6	25.6
Cerium	49.6	49.8	0.4		45	38.8	34.6	21
Praseodymium	4.1	5.15	0.7		5.0	4.4	3.5	5
Neodymium	11.2	15.4	3.0		19	15.4	12.7	12.1
Samarium	0.9	1.15	2.8		3.0	2.1	2.5	5
Europium	0.1	.19	0.1		0.2	0.3	0.3	0.7
Gadolinium	0.2	0.4	6.9		2.6	1.5	2.8	2.4
Terbium	0.0	0	1.3	Heavy Lanthanides	.29	0.3	0.5	0.7
Dysprosium	0.0	0.3	6.7		1.1	1.5	2.8	2.8
Holmium	0.0	0	1.6		.13	0.3	0.5	0.7
Erbium	0.0	0	4.9		.27	0.8	1.8	3.6
Thulium	0.0	0	0.7		.02	0.1	0.2	0.3
Ytterbium	0.0	0	2.5		.12	0.9	1.5	1.4
Lutetium	Trace	0	0.4		.02	0.1	0.2	0.5
Yttrium	0.1	0.2	65.0		3.3	5.7	17.5	18
Scandium	0.0	0.0	Trace		Trace	Trace	Trace	0.5
Percent Heavy	**0.0%**	**0.3%**	**18.1%**		**4.7%**	**4%**	**7.5%**	**10%**
Heavy + Y	**0.1%**	**0.5%**	**83.1%**		**8%**	**9.7%**	**25%**	**28.5**
RE in Ore	8%	5%	0.2%		+50%	12%	3%	3%
Percent Th	0.1%	0.3%	>.1%		8%	3.5%	1%	10.5%***

USGS Data - In order of Geologic Occurrence – Bastnaesite, HRE Laterite, Monazite, Apatite

*Pea Ridge RE resources: Breccia Pipes (primarily Monazite / limited Xenotime).
**Rare Earth Enriched Apatite (Monazite / Xenotime), a no-cost byproduct of iron ore mining.
***Total Actinides = Thorium and Uranium (USGS data), but totals 2 times U.S. annual rare earth demand.

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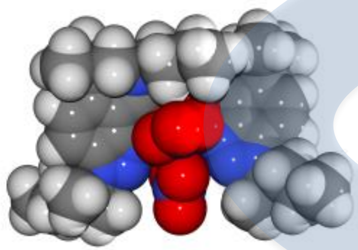
http://www.thoriumenergyalliance.com/

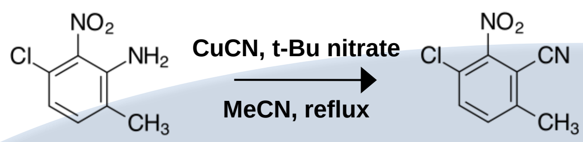
FA1 VISION IS GREAT SCIENCE TO COMMERCIALIZED TECHNOLOGIES

Eight projects focus on reducing supply risk of critical materials

Theory

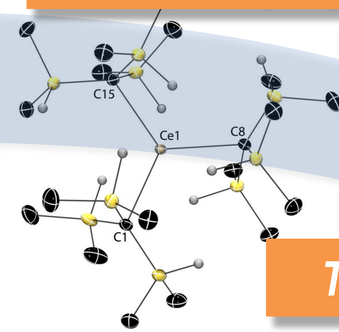
Computations





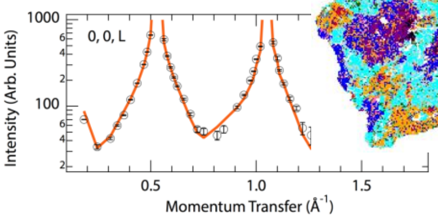
Synthesis

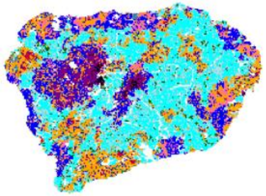
Structure/properties



Testing

Characterization





Commercialized new extractants and processes

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Focus area divided into three thrusts

Industrial partners are actively engaged

- **Molycorp—ore beneficiation, separations, metal conversion**
  - Hosted two tours of Mtn Pass; seminar at Ames
  - Provided samples of bastnaesite flotation concentrate
- **Simbol Materials—recovery of Li from brine**
  - Leading a project
  - Hosted CMI researcher and provided facilities tour
  - Provided Li_2CO_3 samples
- **Cytec—ore beneficiation, separations, phosphate processing, ionic liquids**
  - Hosted a workshop and facility tour
  - Provided samples of ionic liquids and extractants
  - Working directly with CMI researchers at INL on flowsheet tests
- **FIPR—RE recovery from phosphate ore**
  - Industry workshop and facility tour
  - Two tours of Florida phosphate processing plants
  - Provided samples of process phosphoric acid
- **Dow Chemical—RE catalysts**
  - Hosted CMI researcher visit and facility tours