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Kenneth Green,
Environmental Control Technician III,
State of Delaware's Department of Natural Resources and Environmental Control

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Thursday, June 26, 2014

Drug Discovery Series

"Tips for Filing IND and Starting your Clinical Trials"

Dr. Lynn Gold, Camargo Pharmaceutical Services

Dr. John Morrison, Bristol-Myers Squibb

Thursday, July 10, 2014

Strategies for Applying to Grad School

Sam Pazicni, Assistant Professor of Chemistry, University of New Hampshire

Patricia Simpson, Director of Academic Advising and Career Services, University of Illinois Urbana Champaign

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Thursday, September 4, 2014

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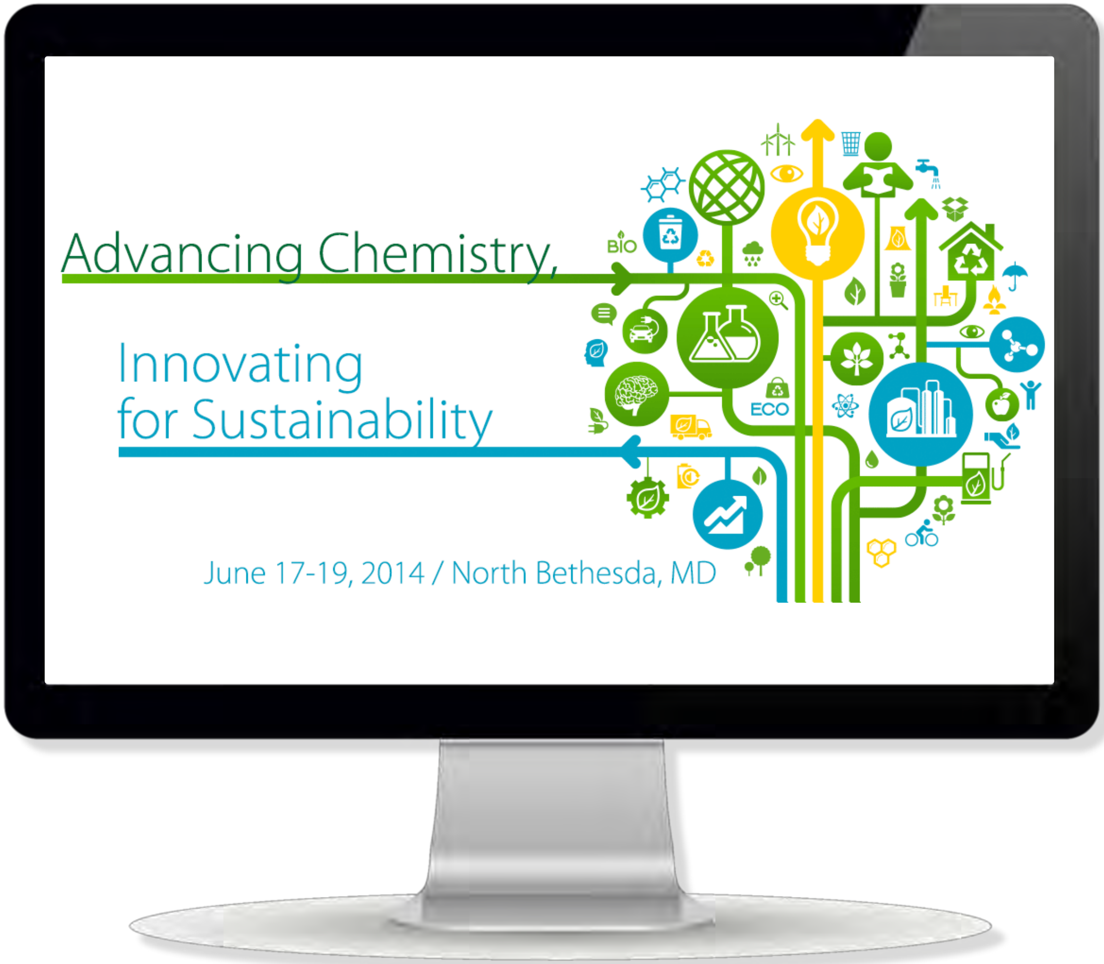

http://www.acs.org/content/acs/en/greenchemistry.html

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ACS Chemistry for Life®

Endangered Elements:
Critical Materials in the Supply Chain

Dr. Roderick Eggert
Critical Materials Institute,
Colorado School of Mines

Dr. Paul Chirik
Princeton University

Dr. Avtar Matharu
Green Chemistry Centre of
Excellence, University of York

Dr. David Constable
ACS Green Chemistry Institute

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Critical Elements and Modern Materials: Economic and Policy Perspectives

Roderick G. Eggert

Professor, Colorado School of Mines, and
Deputy Director, Critical Materials Institute
reggert@mines.edu

ACS Green Chemistry Institute
Bethesda, Maryland, June 19, 2014

COLORADOSCHOOLOFMINES
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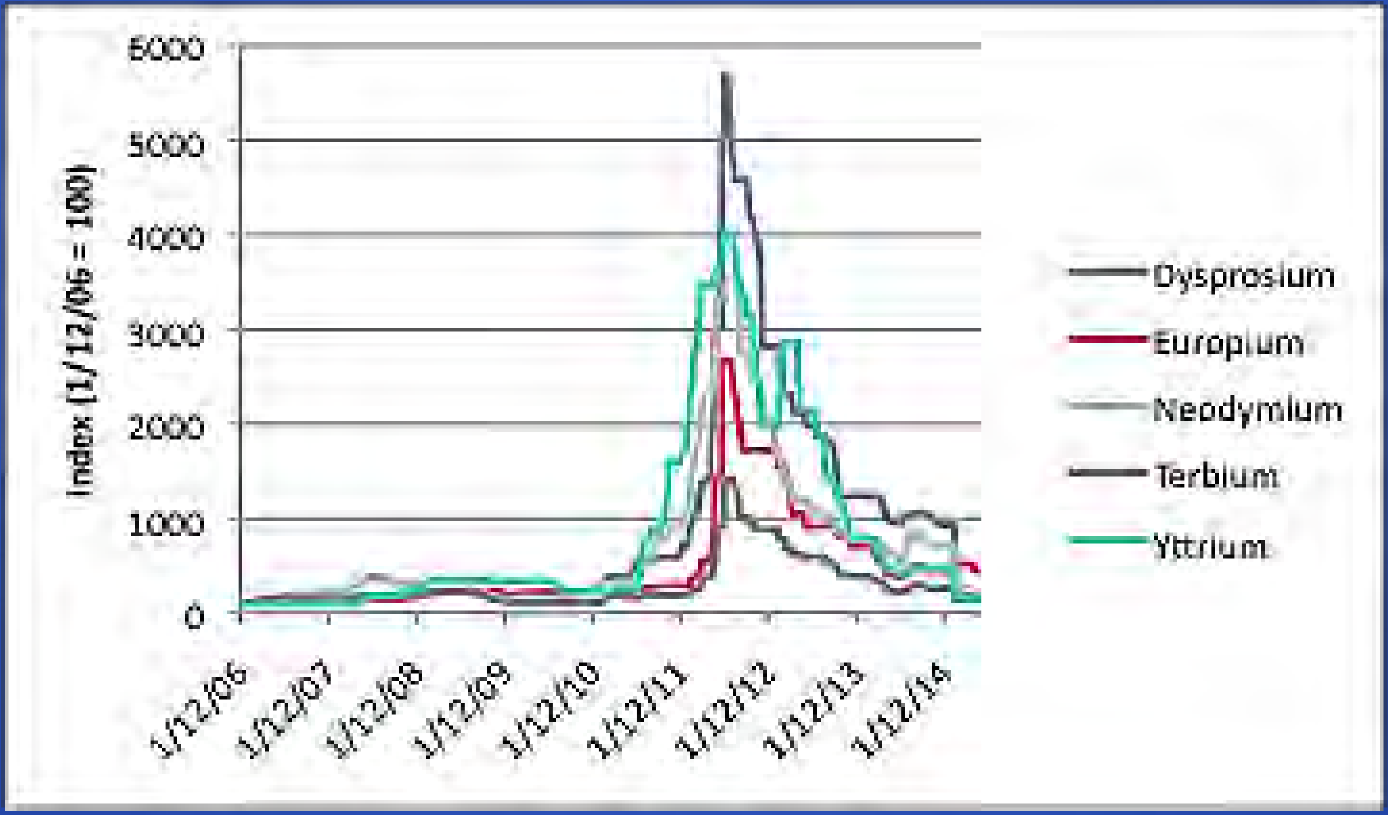
CMI Critical Materials Institute

Index of rare-earth oxide prices, FOB China

(6 January 2006 – 10 June 2014)



Source: metal-pages.com

Starting points

- 'The periodic table is under siege'
- Observations
  - Demand growing quickly. . .supply is fragile:
    - Insecure, or
    - Slow to catch up with demand growth, or
    - Constrained by fundamental geochemical scarcity
  - Leading to high or volatile prices, physical unavailability (or both)
- 'Critical' element: essential in use, subject to supply risk

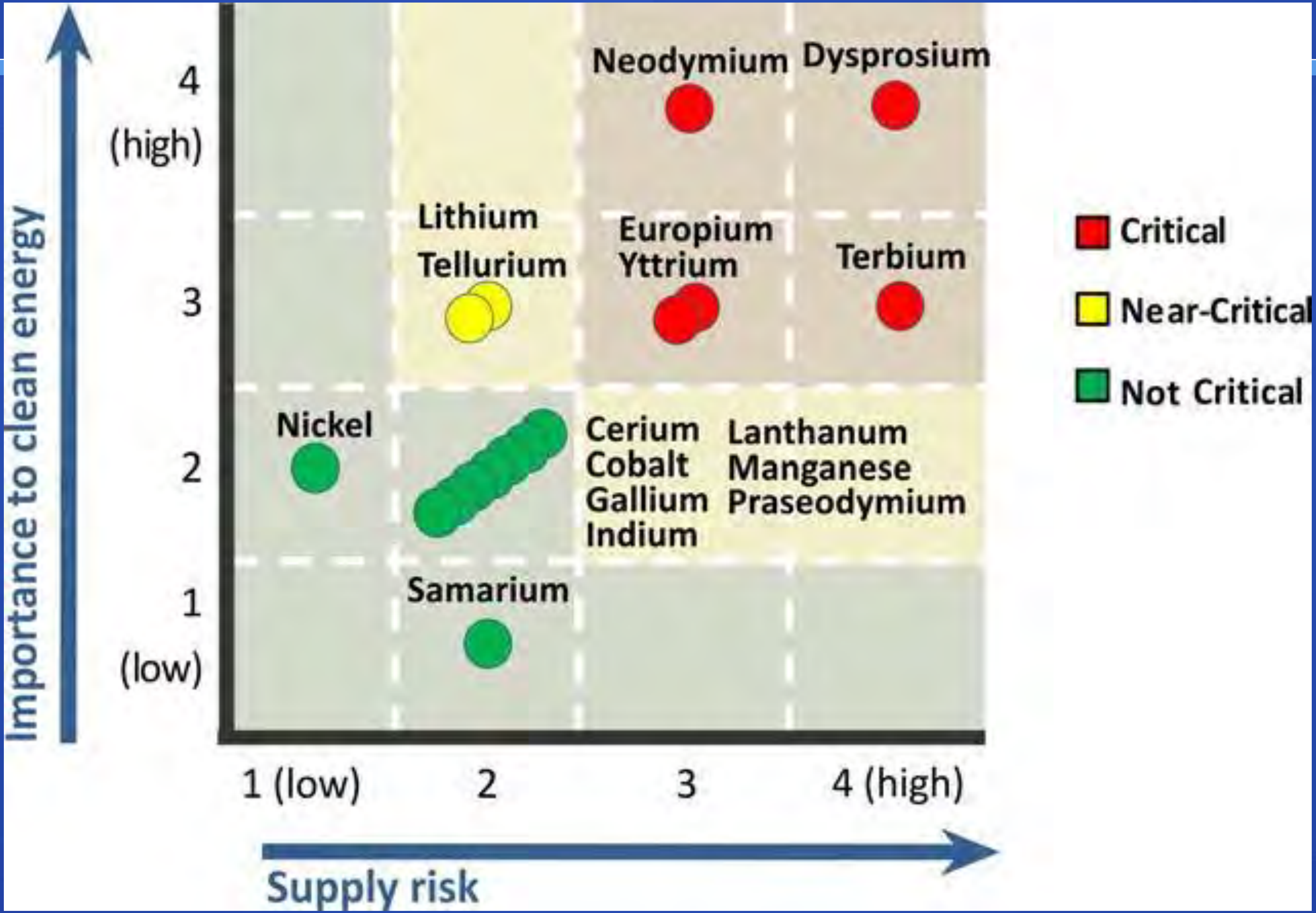
Outline

- Starting points
- The broader context
- What to do?

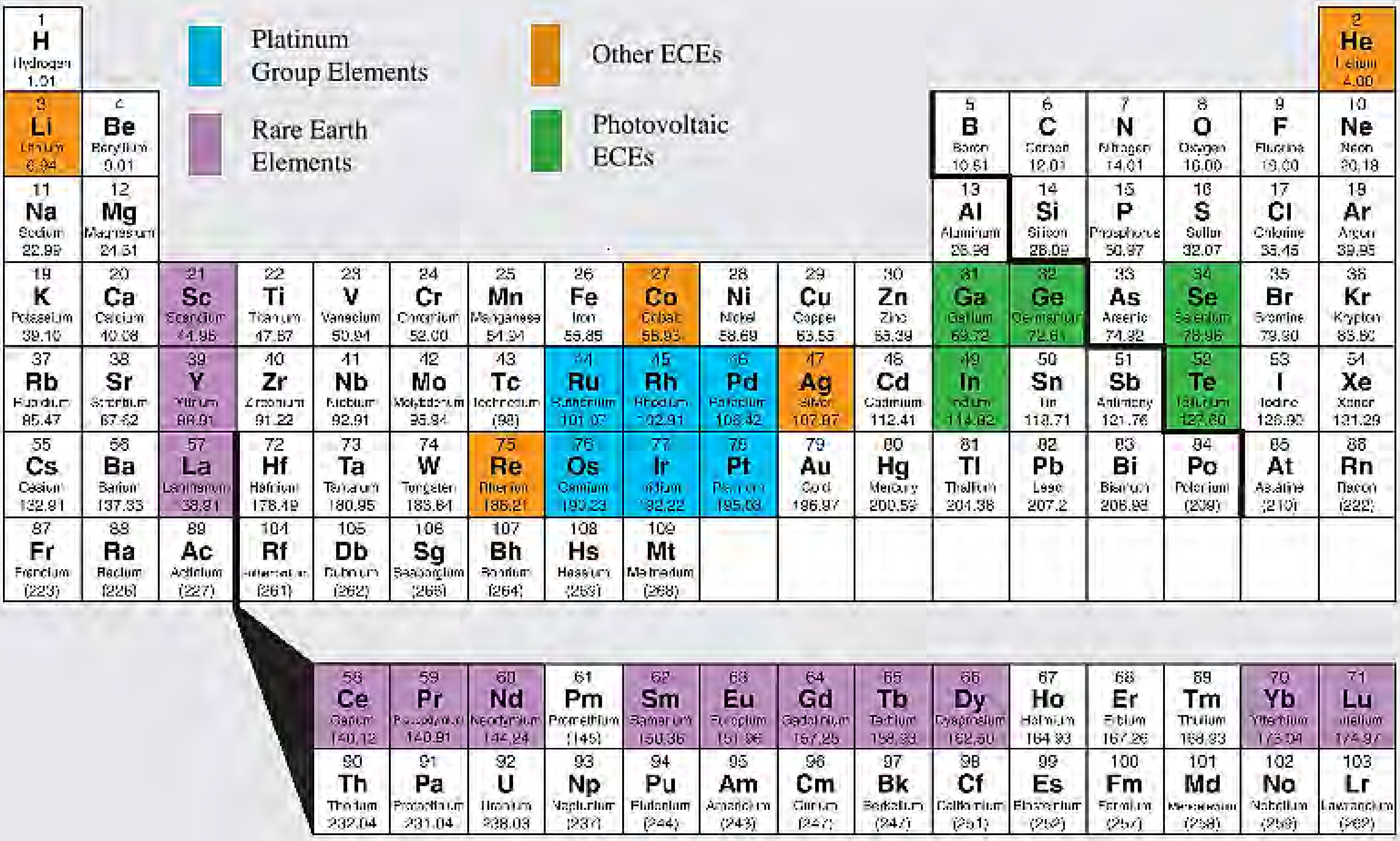
Broad Context

- Criticality is in the eye of the beholder

U.S. Department of Energy, medium-term assessment, 2015-2025

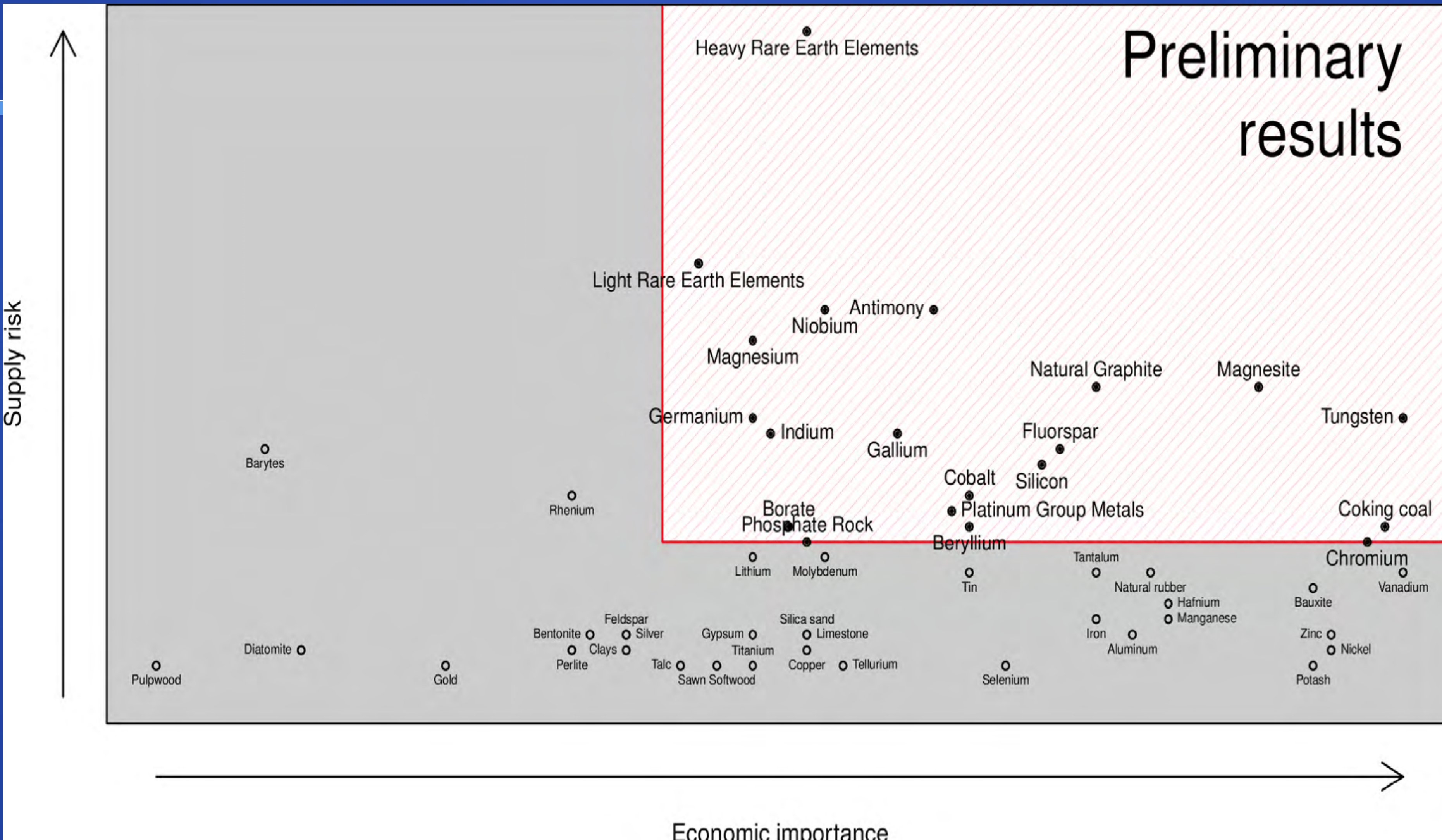


Source: U.S. Department of Energy (2011)



Source: *Energy Critical Elements*, American Physical Society & Materials Research Society, 2011.

European Commission, 2013



Source: Pellegrini, November 2013
(http://ec.europa.eu/enterprise/policies/raw-materials/documents/index_en.htm

Broad Context

- Criticality is in the eye of the beholder
- *We are not 'running out'*

Broad Context

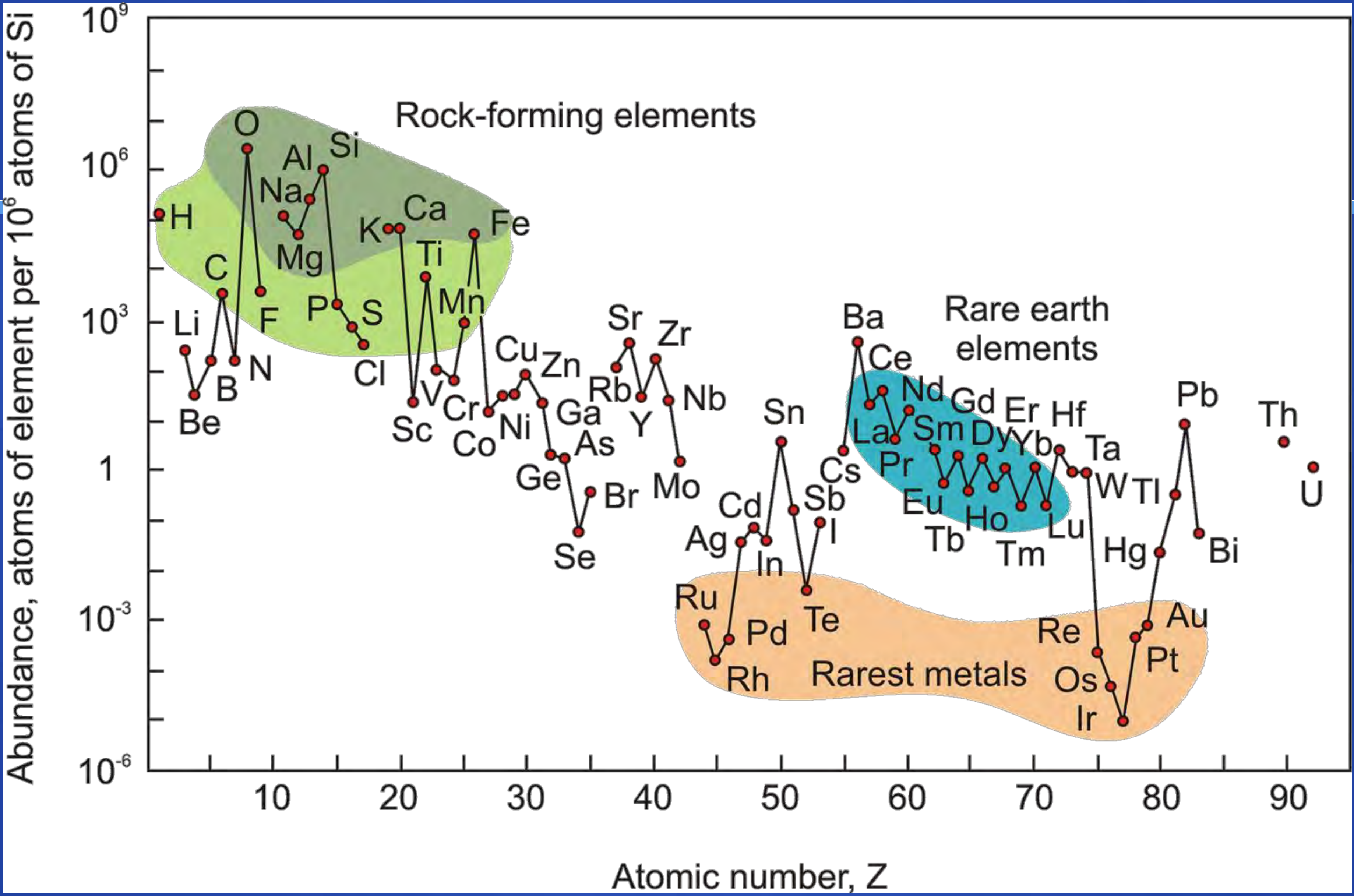
- Criticality is in the eye of the beholder
- We are not 'running out'
- *Each element has its own story*

Each element has its own story…

- Concentrated production: small number of mines, companies, or countries
  - Sometimes linked with geopolitical risks
  - Import dependence is the wrong way to measure risk
  - e.g., Be, rare earths, platinum group

Each element has its own story…

- Concentrated production
- ***Geologic scarcity***
  - *average crustal abundance*
  - *nuances*
    - *degree of concentration above the average by geologic processes*
    - *extent of historical exploration*
  - *e.g., Re, Rh, Te*



Source: U.S. Geological Survey

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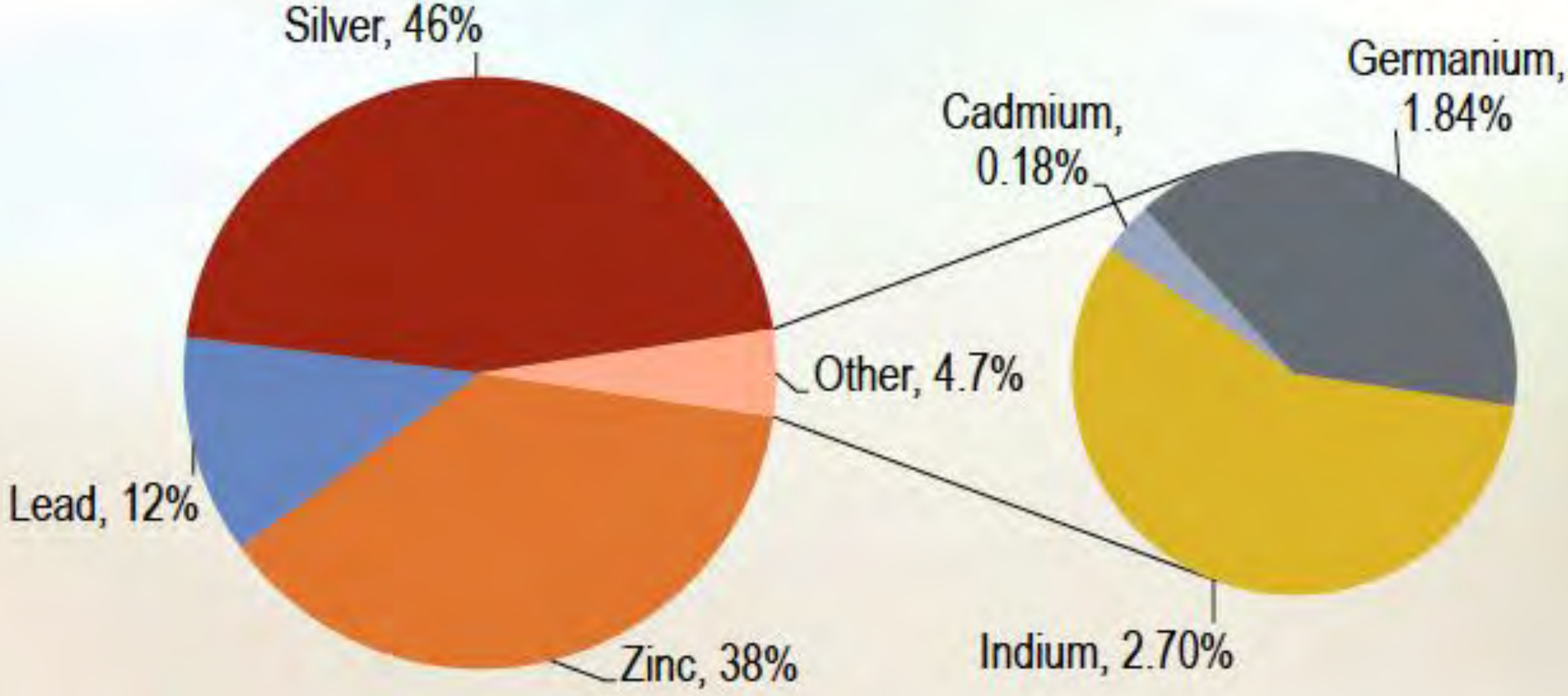
Each element has its own story…

- Concentrated production
- Geologic scarcity
- *Reliance on byproduct production*
  - *Supply may be (a) unresponsive to increased price of byproduct and (b) very responsive to reduced price of main product*
  - *e.g., In/Zn, Te/Cu, Ga/bauxite*

Economics: Lead and Zinc

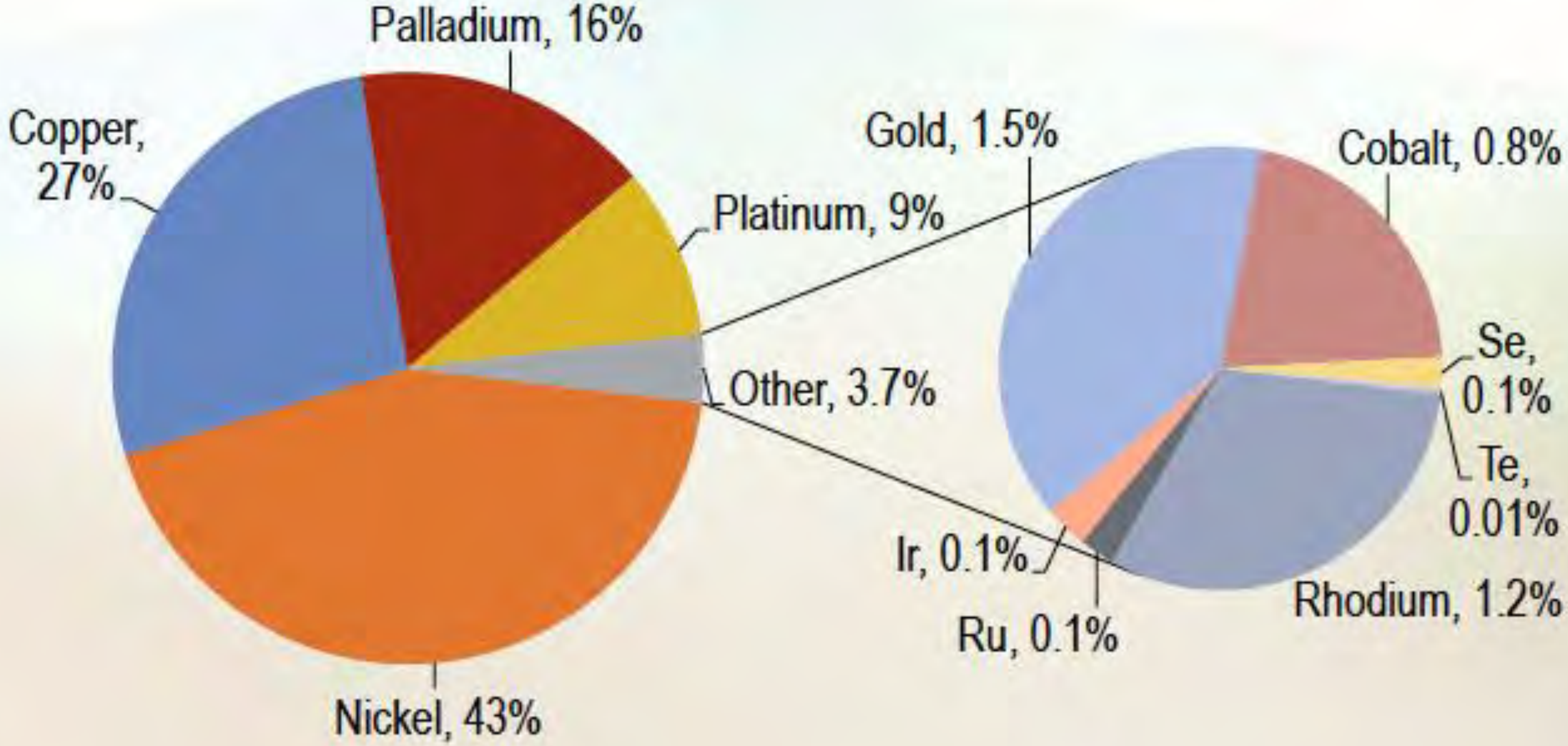
Estimated revenues of Teck Trail Refinery, Canada, 2011



Source: By-products Report

Economics: Nickel and Copper

Estimated revenues of Norilsk Russian Operations, 2011



Source: By-products Report

Broad Context

- Criticality is in the eye of the beholder
- We are not 'running out'
- Each element has its own story
- *Criticality is dynamic—what is critical today may not be critical tomorrow (and vice versa)*

Ammonia: Critical Material of 1898

Gunpowder

Fertilizer

Food Global Population, on Track to Exceed 2,000,000,000

Food Production (Wheat) in Concentrated Locations (US)

$$N_2 + 3H_2 \rightarrow 2NH_3$$

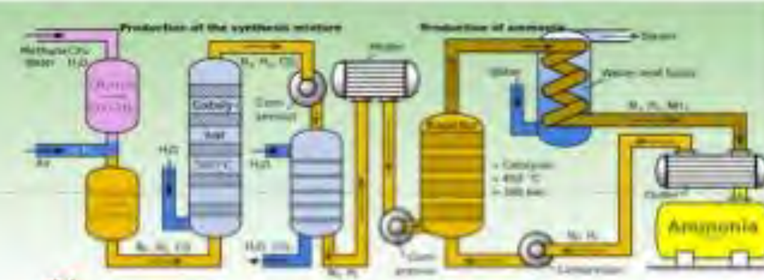
$$\Delta G^{\circ}(J) = -87{,}030 + 5.8T\ln T + 31.7T$$

"…the fixation of Nitrogen is vital to the progress of civilized humanity"
William Crookes (1898)

Advanced Research Projects Agency • Energy

Source: Mark Johnson (DOE)

Ammonia R&D



Royal Academy "Wheat Problem" — Understanding Properties Of Ammonia — Academic Fight — Contract — Lab Demo — Pilot Scale — Production

"Grand Challenge" – – Basic Research – – – – – – ◆ Break-Through ◆— "Catalyst Genomics" →

1898 | 1900 | 1902 | 1904 | 1906 | 1908 | 1910 | 1912 | 1914

Crookes

Ostwald & Nernst

Haber

Bosch

Mittasch

arpa·e Advanced Research Projects Agency • Energy

U.S. DEPARTMENT OF ENERGY

Source: Mark Johnson (DOE)

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Broad Context

- Criticality is in the eye of the beholder
- We are not 'running out'
- Each element has its own story
- Criticality is dynamic—what is critical today may not be critical tomorrow (and vice versa)
- ***Small, fragmented, non-transparent markets → volatility; risks to investors, producers and users***

Outline

- Starting points
- The broader context
- ***What to do?***

Allow markets to work, recognize time lags

- Markets provide powerful incentives
- Supply side
  - Exploration
  - Byproducts become main products
  - R&D on extraction technologies, manufacturing efficiency, recycling
  - NOTE: recycling alone will not save us

Allow markets to work, recognize time lags

- Markets provide powerful incentives
- Supply side
- Demand side: insurance
  - Short term: working inventories, diversified supply, sharing arrangements with other users, strategic relationships with suppliers
  - Long term: element-for-element substitution, system substitution

Recognize essential roles for government

- Pushing for undistorted international trade
- Improving the process of regulatory approval for domestic resource development
- Facilitating research and education over the entire supply chain
  - Geoscience → mining, mineral processing, extractive metallurgy → materials → recycling

Final Thoughts

- A critical element is: important in use, subject to supply risk
- We are not 'running out'; other risks more significant
- Markets provide powerful incentives, but market responses take time
- There are essential roles for government

References and Additional Information

Critical Raw Materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials, European Commission, 30 July 2010.

Eggert, Roderick G. "Critical Minerals and Emerging Technologies," *Issues in Science and Technology*, Summer 2010, pp. 49-58.

Eggert, Roderick G. "Minerals go critical," *Nature Chemistry*, vol. 3, September 2011, pp. 688-691.

Energy Critical Elements: Securing Materials for Emerging Technologies, a report by the APS Panel on Public Affairs and the Materials Research Society (American Physical Society and Materials Research Society, 2011).

National Research Council. *Minerals, Critical Minerals, and the U.S. Economy* (Washington, DC, National Academies Press, 2008).

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Parthemore, Christine. *Elements of Security: Mitigating the Risks of U.S. Dependence on Critical Materials* (Washington, D.C., Center for a New American Security, 2011).

Pellegrini, Mattia. Presentation at the US-Europe workshop on material flows, November 2013, Pellegrini, November 2013, http://ec.europa.eu/enterprise/policies/raw-materials/documents/index_en.htm.

Oakdene Hollins. *Study of By-products of Copper, Lead, Zinc and Nickel*. Prepared for the International Copper Study Group, International Lead and Zinc Study Group, and International Nickel Study Group, June 2012.

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References and Additional Information (continued)

United States Department of Energy, *Critical Materials Strategy*, December 2010.

United States Department of Energy, *Critical Materials Strategy*, December 2011.

United States Geological Survey, *China's Rare-Earth Industry*, Open-File Report 2011-1042.

United States Geological Survey, *The Principal Rare Earth Element Deposits of the United States—A Summary of Domestic Deposits and a Global Perspective*, Scientific Investigations Report 2010-5220.

Endangered Elements in Catalysis

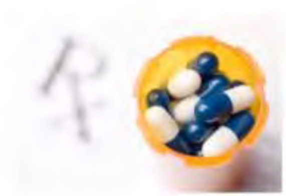
Paul J. Chirik
Department of Chemistry
Princeton University

June 19, 2014

PRINCETON UNIVERSITY

The Importance of Catalysis

Catalysis enables our modern way of life...



Pharmaceuticals

Environment

Energy

Household Items

...and is a key component of sustainable chemistry.

Are all catalytic processes as sustainable as possible?

What processes are the least sustainable? Why?

As chemists, we are always interested in catalysts for new applications.

Dependence on Exotic Elements

In the last 5 years, the average American has relied on **80** elements for quality of life.

General Electric uses **72** of the first **82** elements in its product line.

Pharmaceuticals
Pd, Rh, Os, Ir

Household Items
Rh, Pt

Refining
La, Pt

Hybrid/Electric Cars
Nd, Tb, Dy, Pr

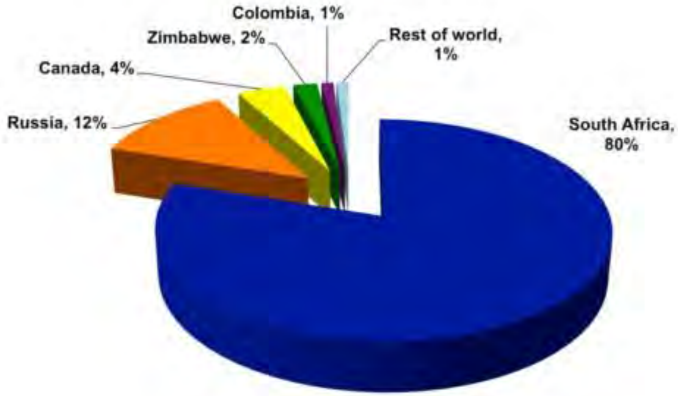
Alternative Energy
Ru, Nd, Tb, Dy, Pr

McGroarty, D. *Wall Street Journal* 1/31/13

Jaffe, R. *2011 APS-MRS Report*

Concerns with Platinum

Sources



All Pt ever mined would fit in a box that is 25 cubic feet!

- 1 ounce of Pt = 10 tons of ore, 1 mile down.
- 130 tons annually = 4.5 million tons of Earth.
- 50% of mined Pt is "lost".
- CO_2 footprint at least 7000x of that for iron.

Not only expensive but volatile...

http://www.zerohedge.com/

Just How Valuable is Platinum?

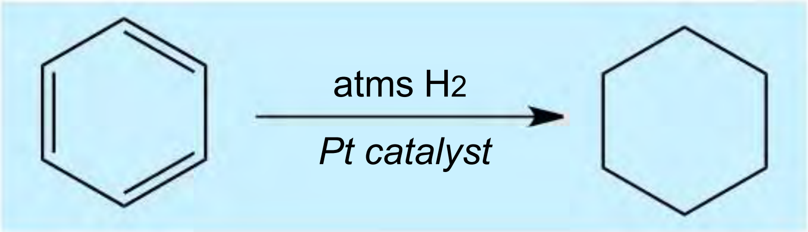
PLANETARY
RESOURCES™

"The Asteroid Mining Company"

See: http://www.bbc.co.uk/news/science-environment-21144769

Comparison of Pt-Catalyzed Reactions

Benzene Hydrogenation: Low Distribution Entropy

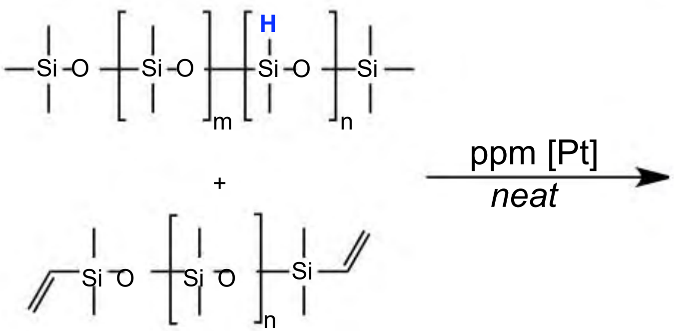


High catalyst recovery

Silicone Release Coatings: High Distribution Entropy

SL 6020

SL 6100

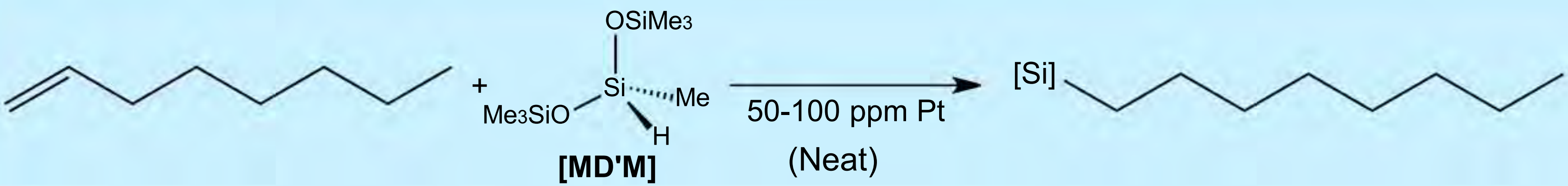


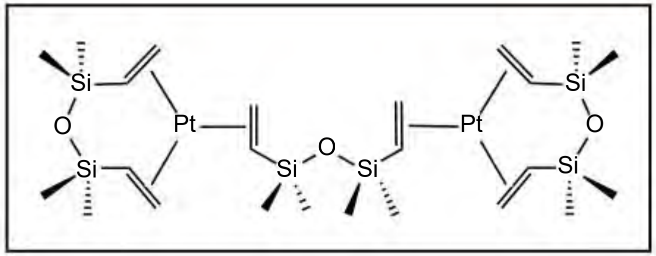
Little to no catalyst recovery.

Residual Pt accounts for 30-40% of the cost of the coating.

This is an application in need of base metals!

More About Platinum Catalyzed Hydrosilylation





"Karstedt's Catalyst"

Byproducts of Hydrosilylation (10-30 %)

From Decomposition to **Pt$_{\textbf{black}}$**

Issues for base metals: cost, selectivity <u>and new reactivity</u>.

Why not base metals? It's all about electrons!

Precious Metals: 2e- chemistry (Oxidative Addition/Reductive Elimination)

Rh(I) ⇄ Rh(III) ⇄ Rh(V)

Base Metals: 1e- chemistry (Radicals, autoxidation)

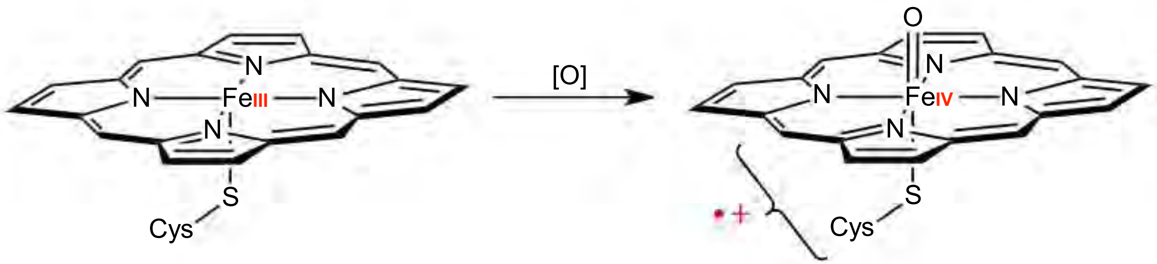
Fe(0) ⇄ Fe(I) ⇄ **Fe(II)** ⇄ **Fe(III)** ⇄ Fe(IV) ⇄ Fe(V) ⇄ Fe(VI)

Fundamental Question:

How do we achieve 2e- chemistry from a 1e- transition metal platform?

How we go about this...

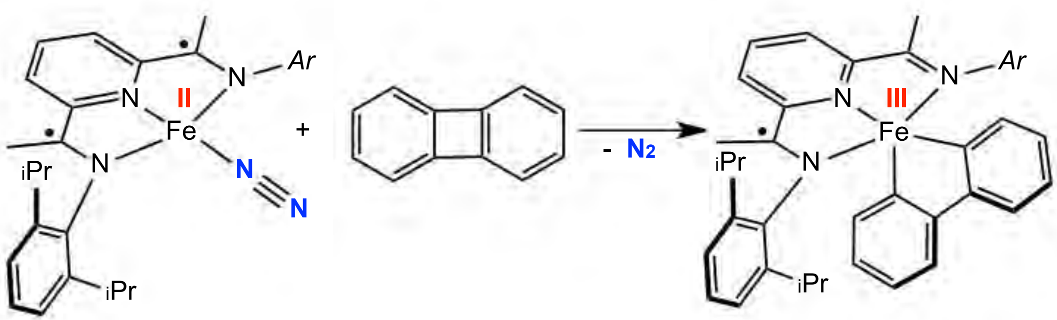
In Enzymes:



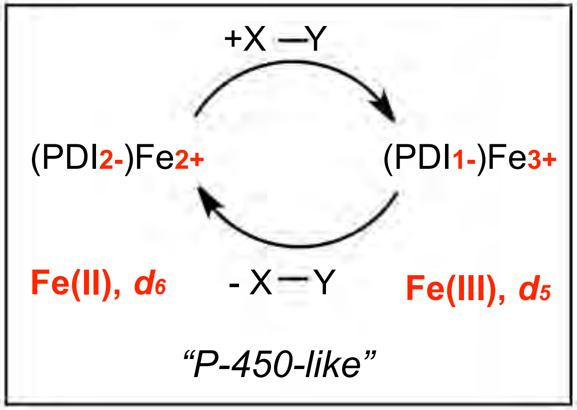
Nature uses "redox active" ligands to achieve 2e- chemistry with base metals.

Green, M. *Science* **2010**, *330*, 933.

Chirik Laboratory:



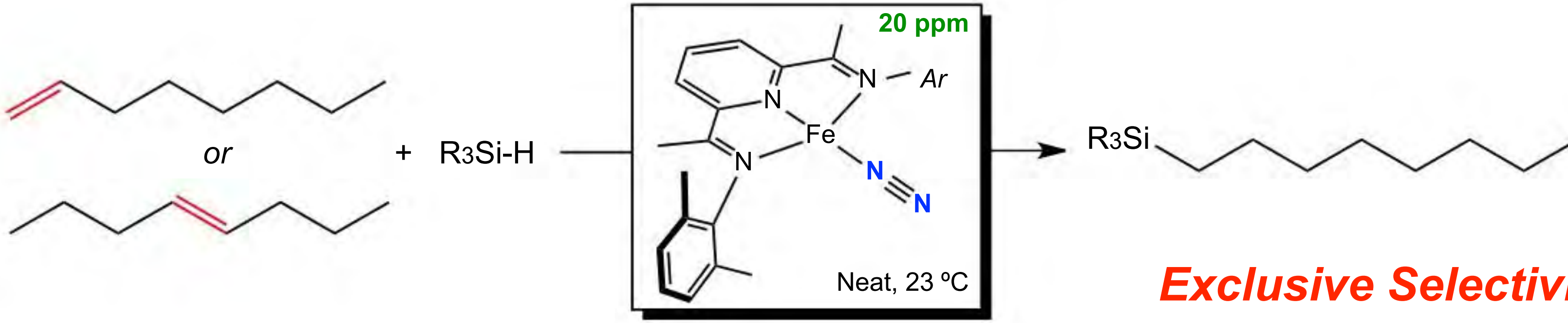
Metal-ligand cooperative oxidative addition.



Can we apply this concept to the synthesis of commercial silicones?

Darmon, Chirik, *et al.* *JACS* **2012**, *134*, 17125.

Iron Catalysts for Hydrosilylation



Exclusive Selectivity

Silicone Fluids:

Pros:
- Base metal catalyst.
- Unprecedented activity and selectivity.

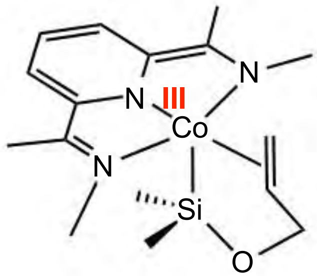
Cons:
- Air-sensitive, fragile catalysts.
- Residual ligand is highly colored.

MOMENTIVE™

Tondreau, Atienza, Chirik, *et al. Science* **2012**, 567.

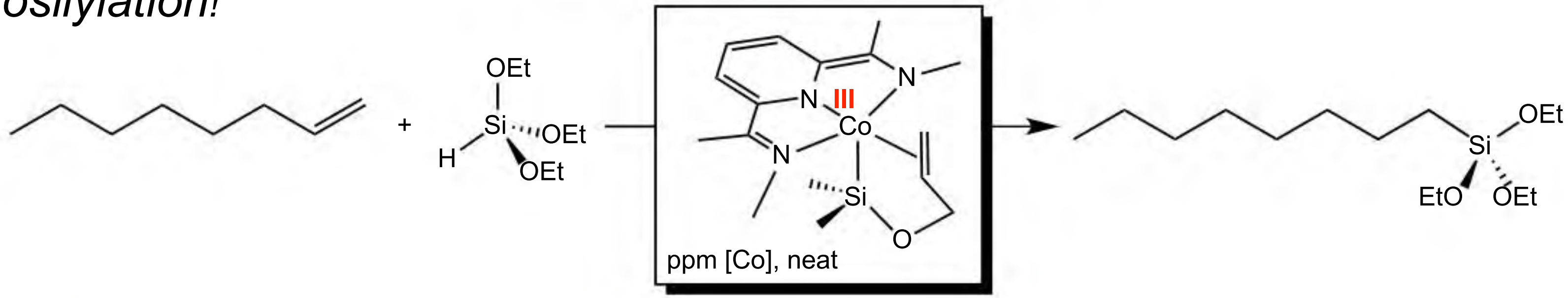
Looking to Cobalt

Lessons from coordination chemistry: Co(III), d^6 is substitutionally inert.



In air!

Hydrosilylation!



Silicone Fluids:

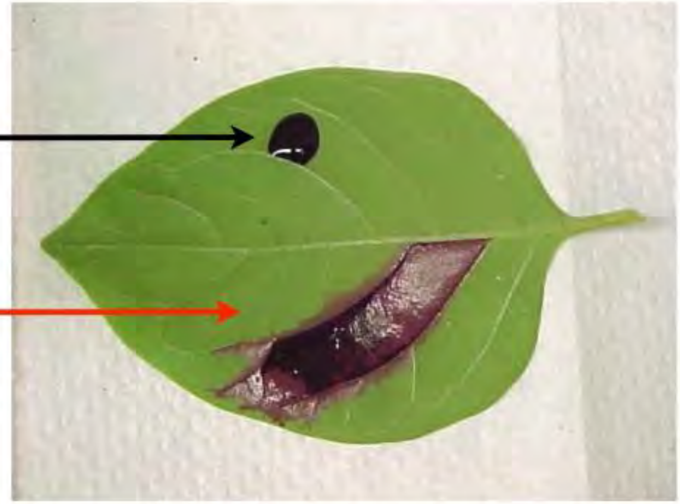
Air Stable Co Catalyst

Catalysis for the Environment

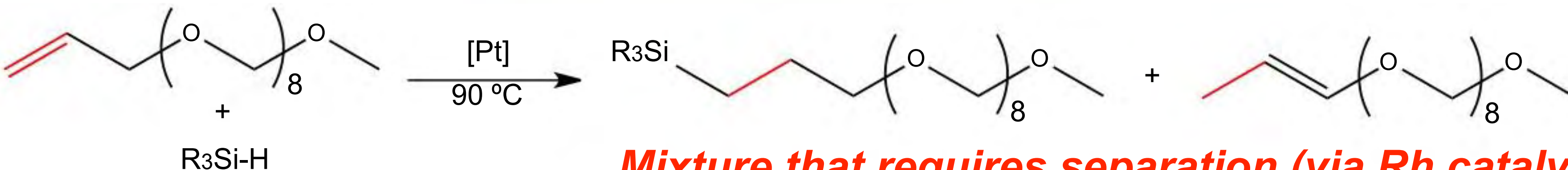
Increased Selectivity For Green Chemistry

No silicone

1 wt% "Super Spreader"

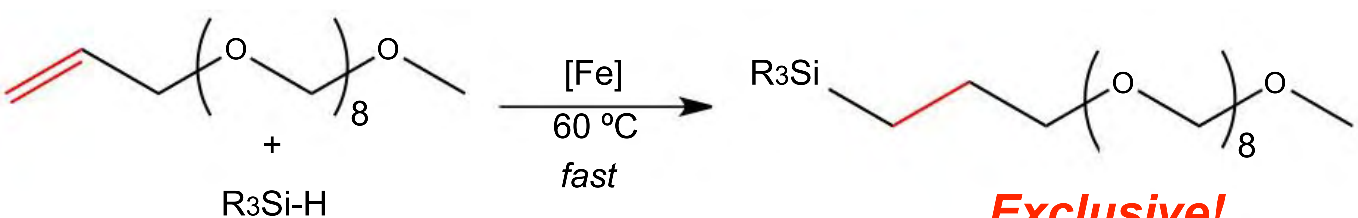


Current Practice:



Mixture that requires separation (via Rh catalysis)

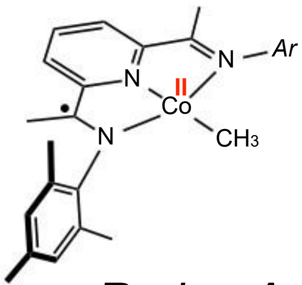
With Iron Catalysis:



Exclusive!

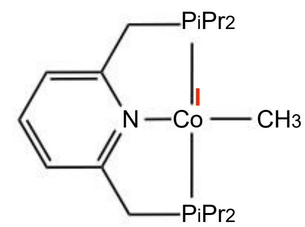
The Consequences of Keeping the Electrons on the Metal

What happens when we confine 2 electron redox to the metal?



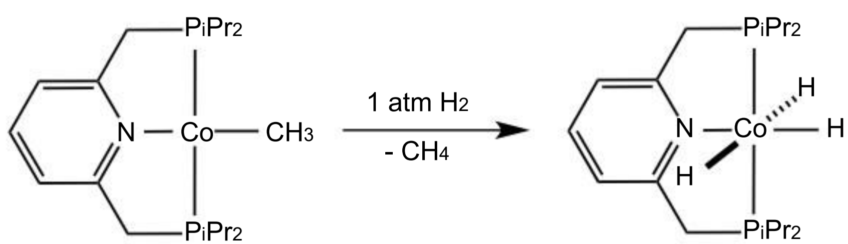
Redox-Active

Remote Hydroboration, hydrosilylation



Classical Co(I), d_8

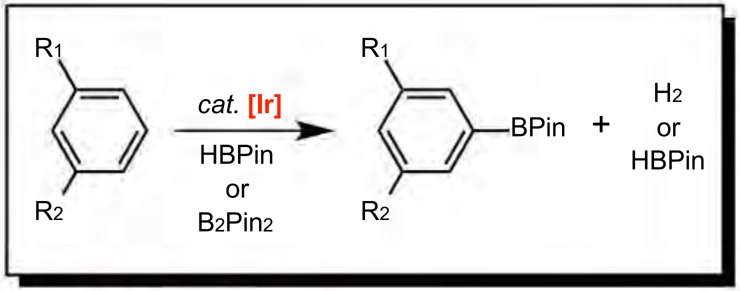
Precious metal-like oxidative addition!



Does this offer new opportunities in catalysis?

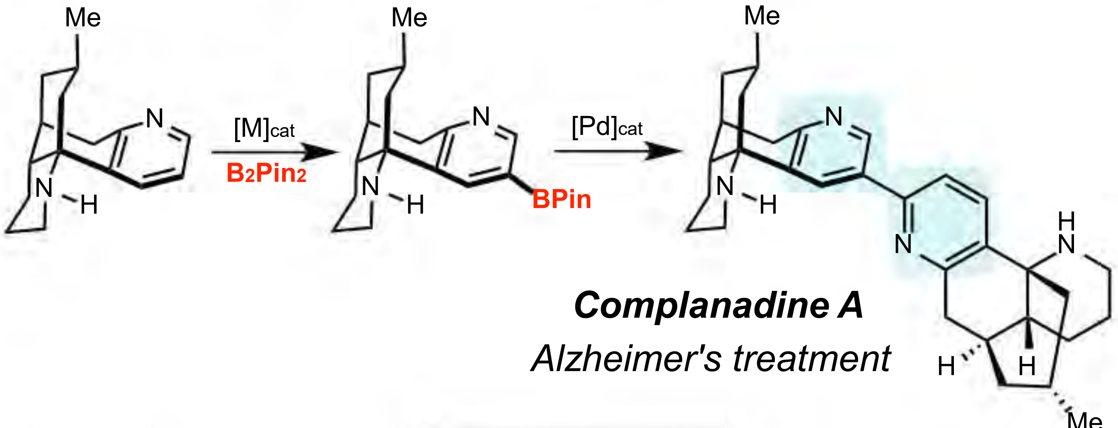
Semproni, Chirik *Chem. Sci.* **2014**, 1956.

Base Metal Catalyzed C-H Functionalization



BoroPharm, Inc. Your Bridge to Discovery   >3000 products

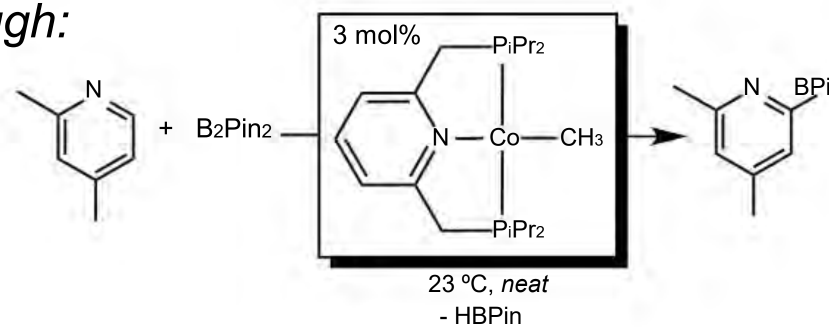
Tool for Med Chem:



Complanadine A

Alzheimer's treatment

Base Metal Breakthrough:

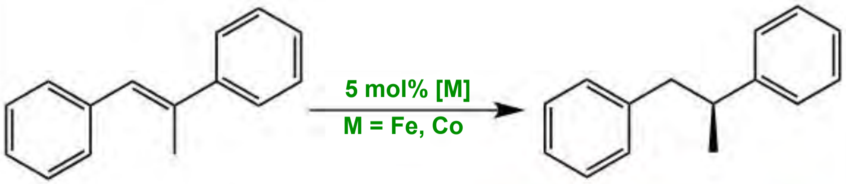


TONs up to 5000 at 0.02 mol% [Co].

Obligacion, Chirik *JACS* **2014**, *136*, 4133.

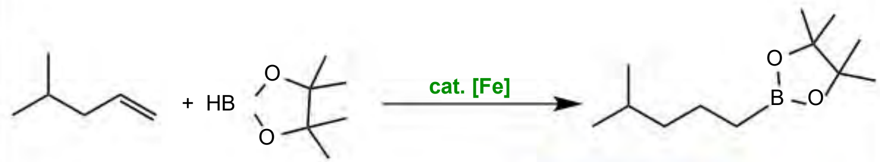
Applications of Our Base Metal Library

Alkene Hydrogenation



Science **2013**, 2, 1076.
J. Am. Chem. Soc. **2013**, *135*, 1316
J. Am. Chem. Soc. **2012**, *134*, 4561.

Hydrofunctionalization

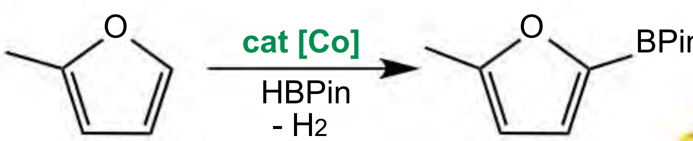


J. Am. Chem. Soc. **2013**, *135*, 19107
Si: *Science* **2012**, *335*,

Cycloaddition

J. Am. Chem. Soc. **2013**, *135*, 4862.
J. Am. Chem. Soc. **2011**, *133*, 8858.

C-H Functionalization Methods



J. Am. Chem. Soc. **2014**, *136*, *ASAP*.

This is only the beginning, we have much to learn and discover!

Base Metal Team

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Merck

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Endangered Elements: Critical materials in the supply chain

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Deputy Director
Green Chemistry Centre of Excellence
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Research

Industry

Networking

Education

What am I? In this year…

http://www.nature.com/nature/journal/v494/n7438/images/494423a-i1.0.jpg

http://periodieksysteem.com/biografie/ferdinand-reich

What am I? In this year…

Audience poll

The year in question and the element discovered is?

1. 1853 and indium
2. 1901 and tungsten
3. 1863 and indium
4. 1799 and indium
5. 1763 and dysprosium

Discovered in 1863

http://periodieksysteem.com/biografie/ferdinand-reich

http://periodictable.com/Elements/049/

I am INDIUM

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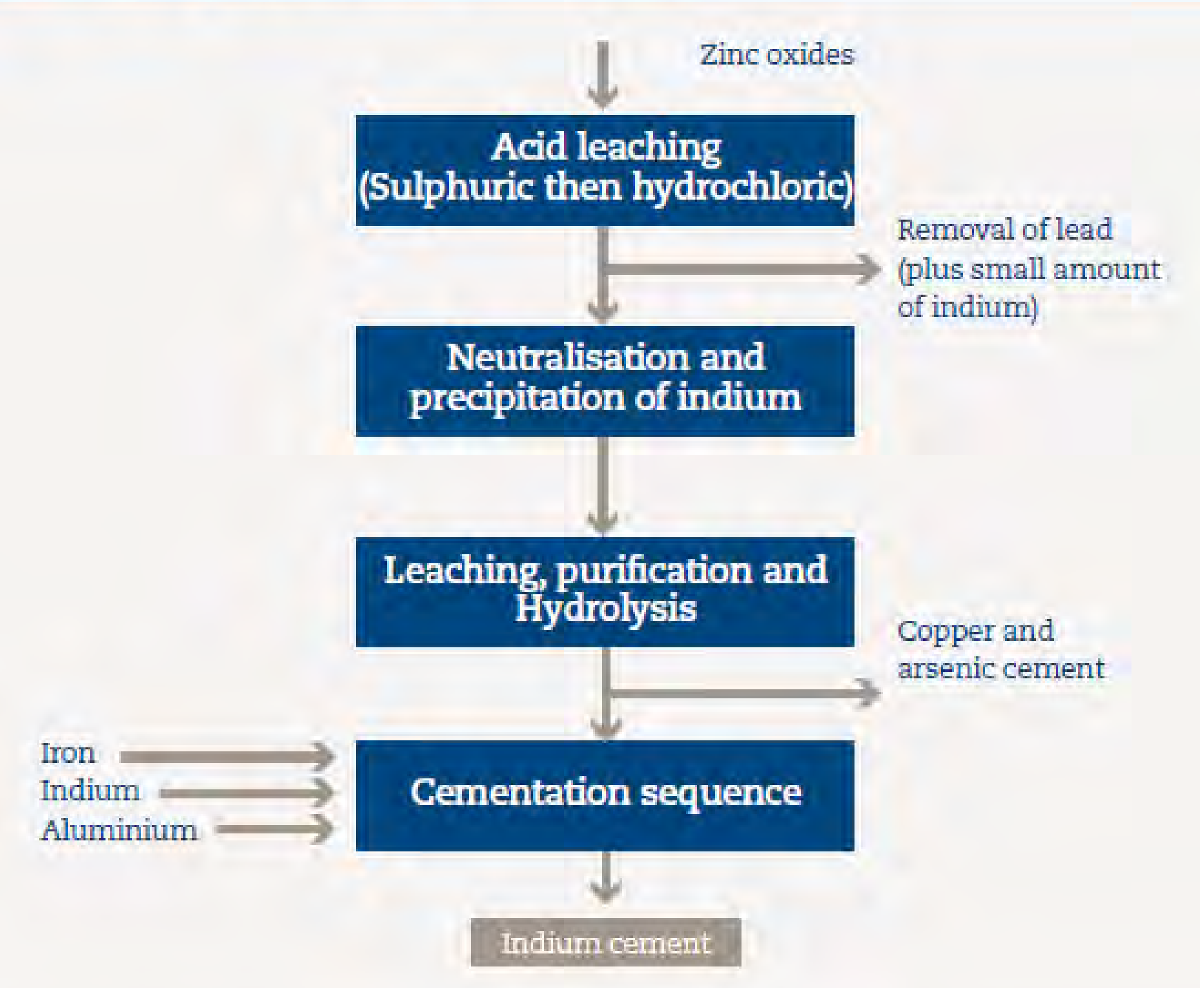
Where from?...

Indium production from Zinc



Source: Ullman & Bohnet (2012)

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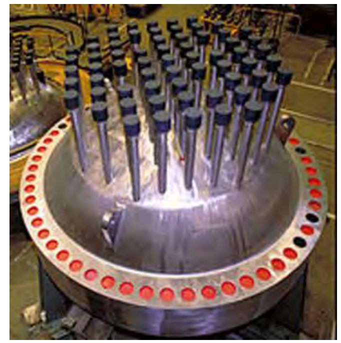
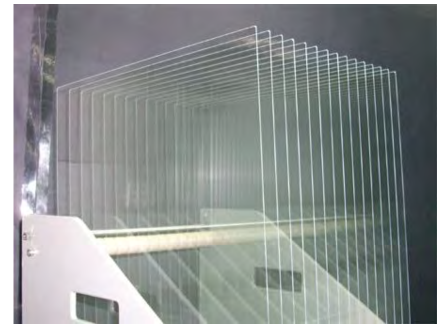
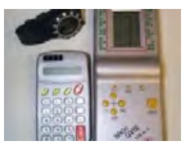
Indium – who cares?

Levels of our dependency







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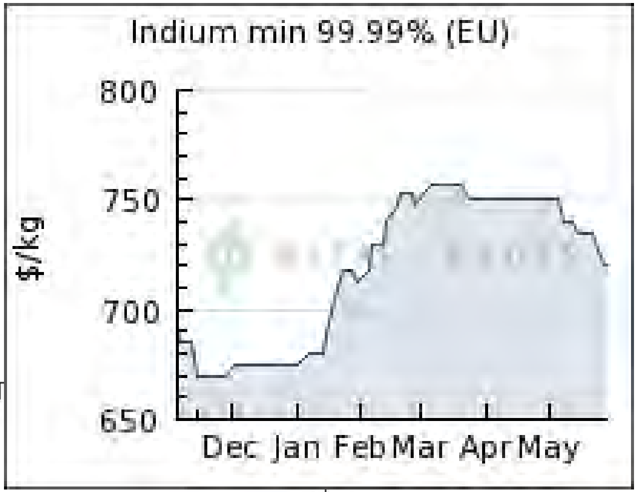
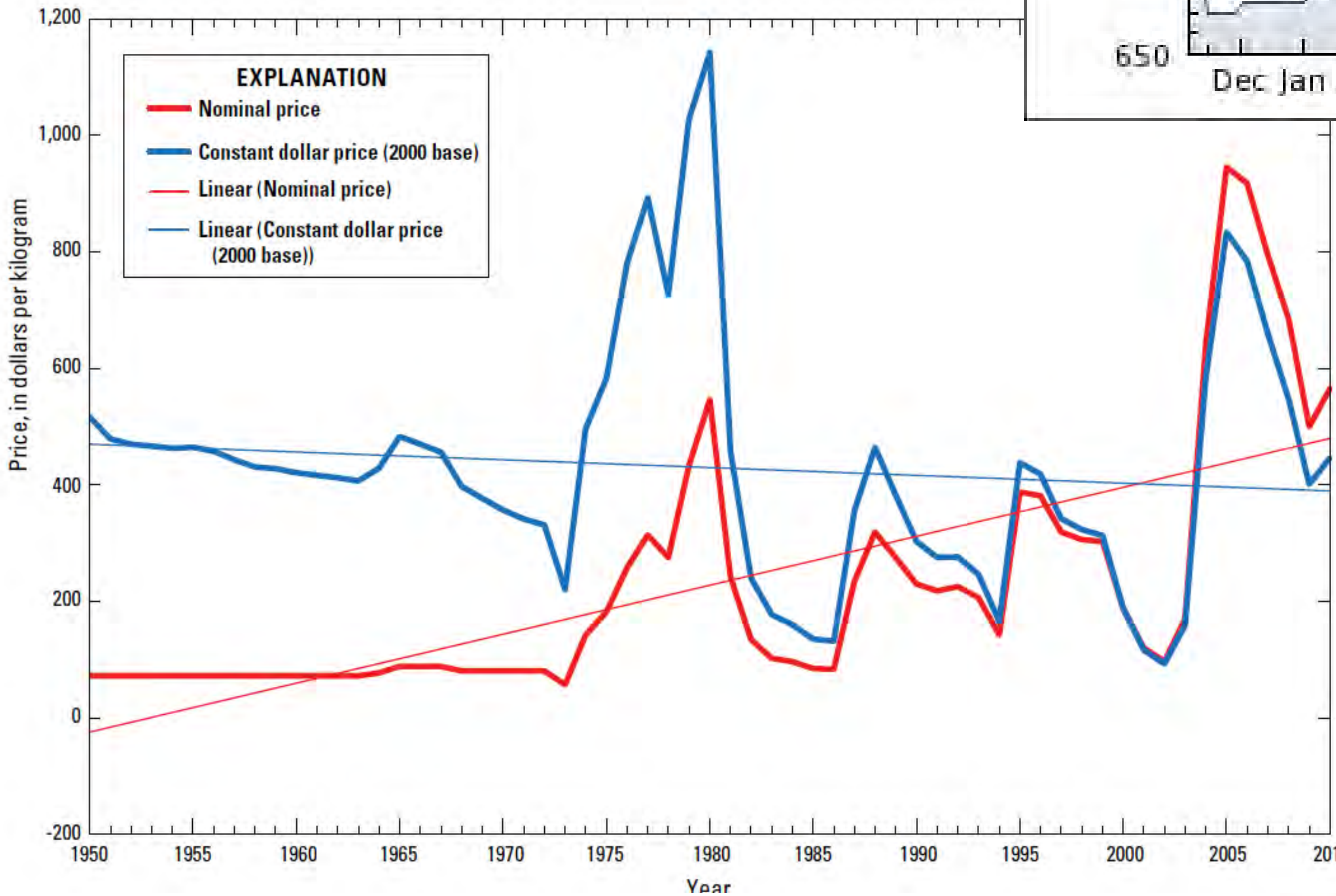
Value or Price?





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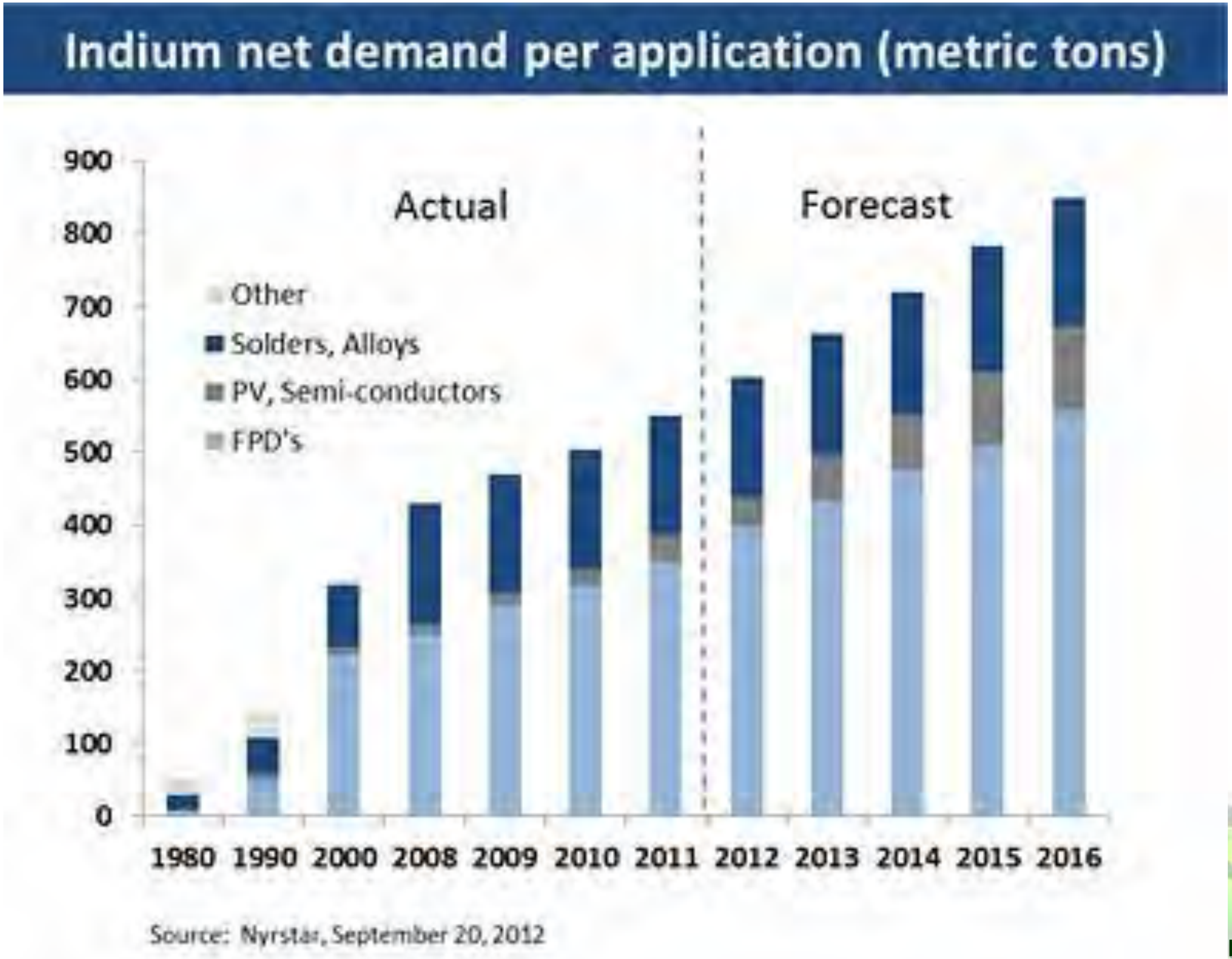
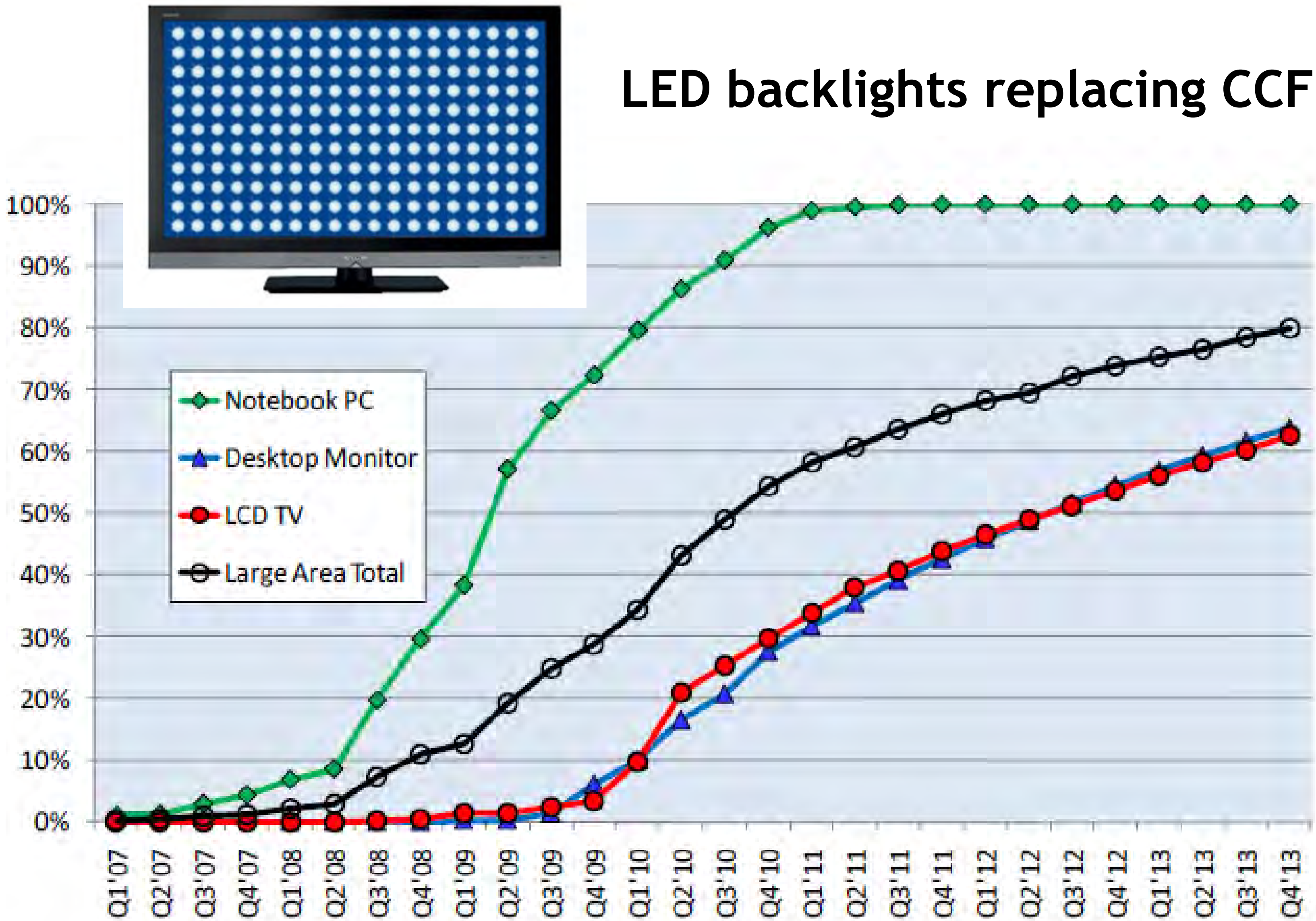
Indium – who cares?

Levels of our dependency



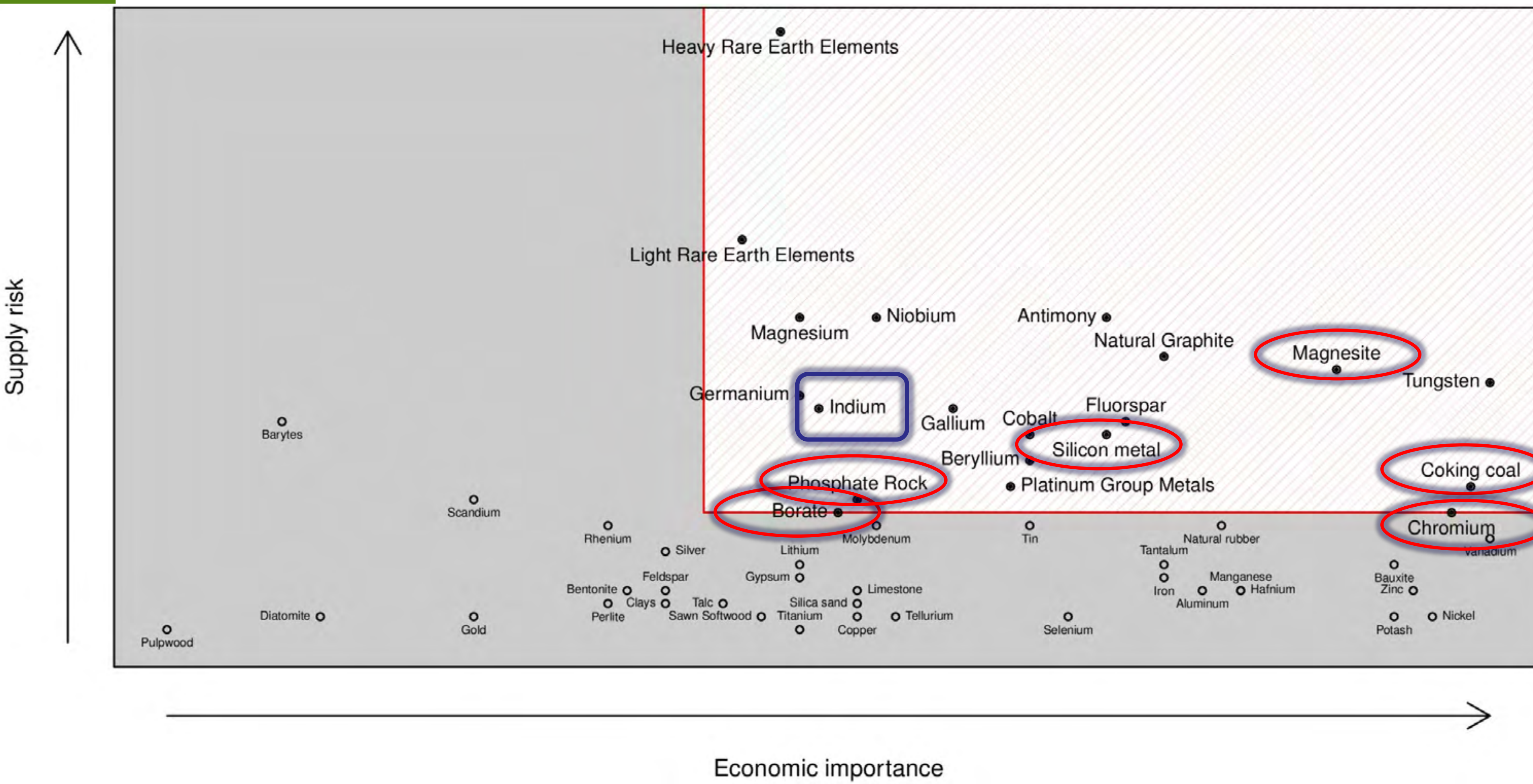
Not just ITO

LED backlights replacing CCFL

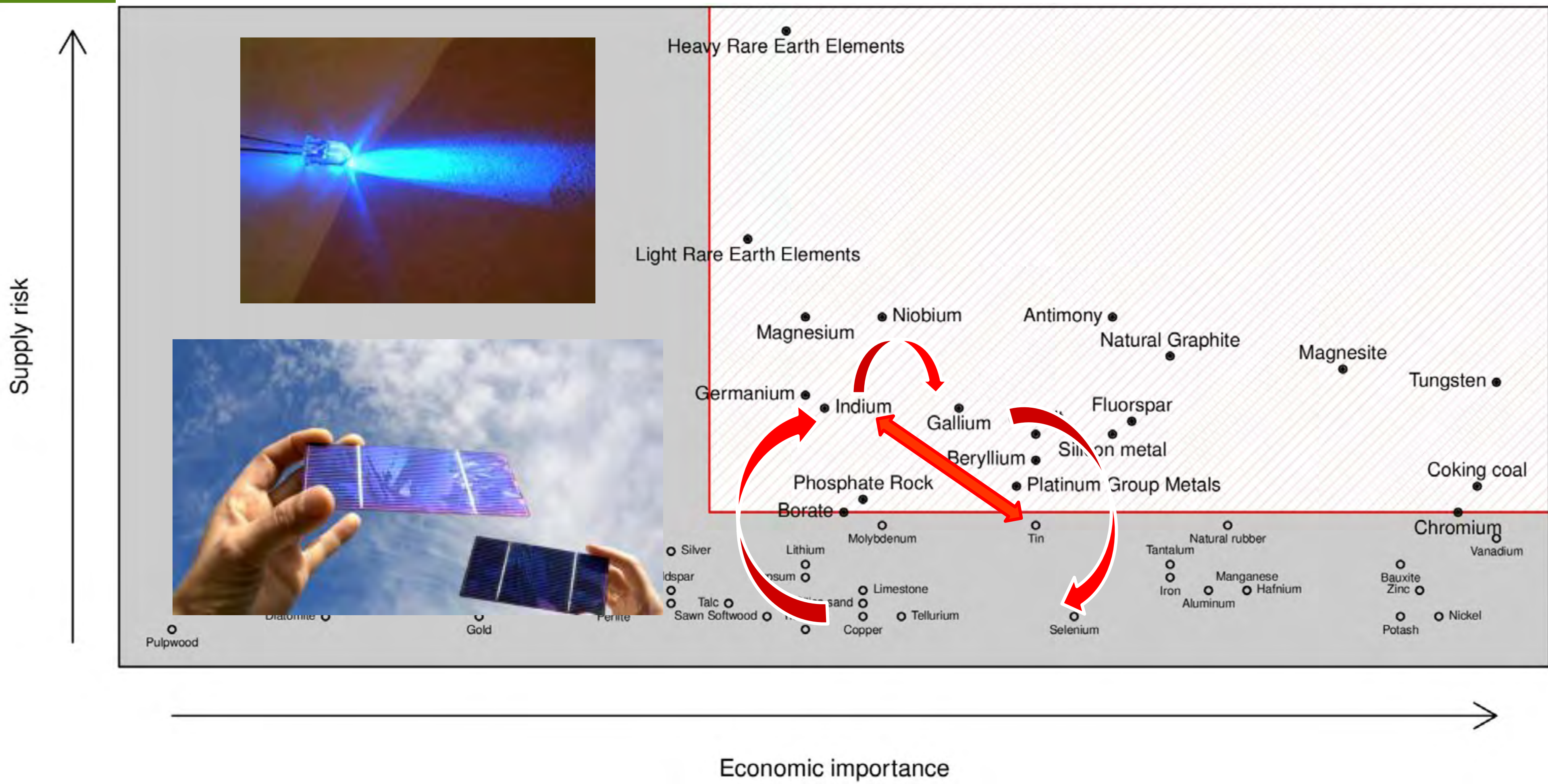


European Perspective

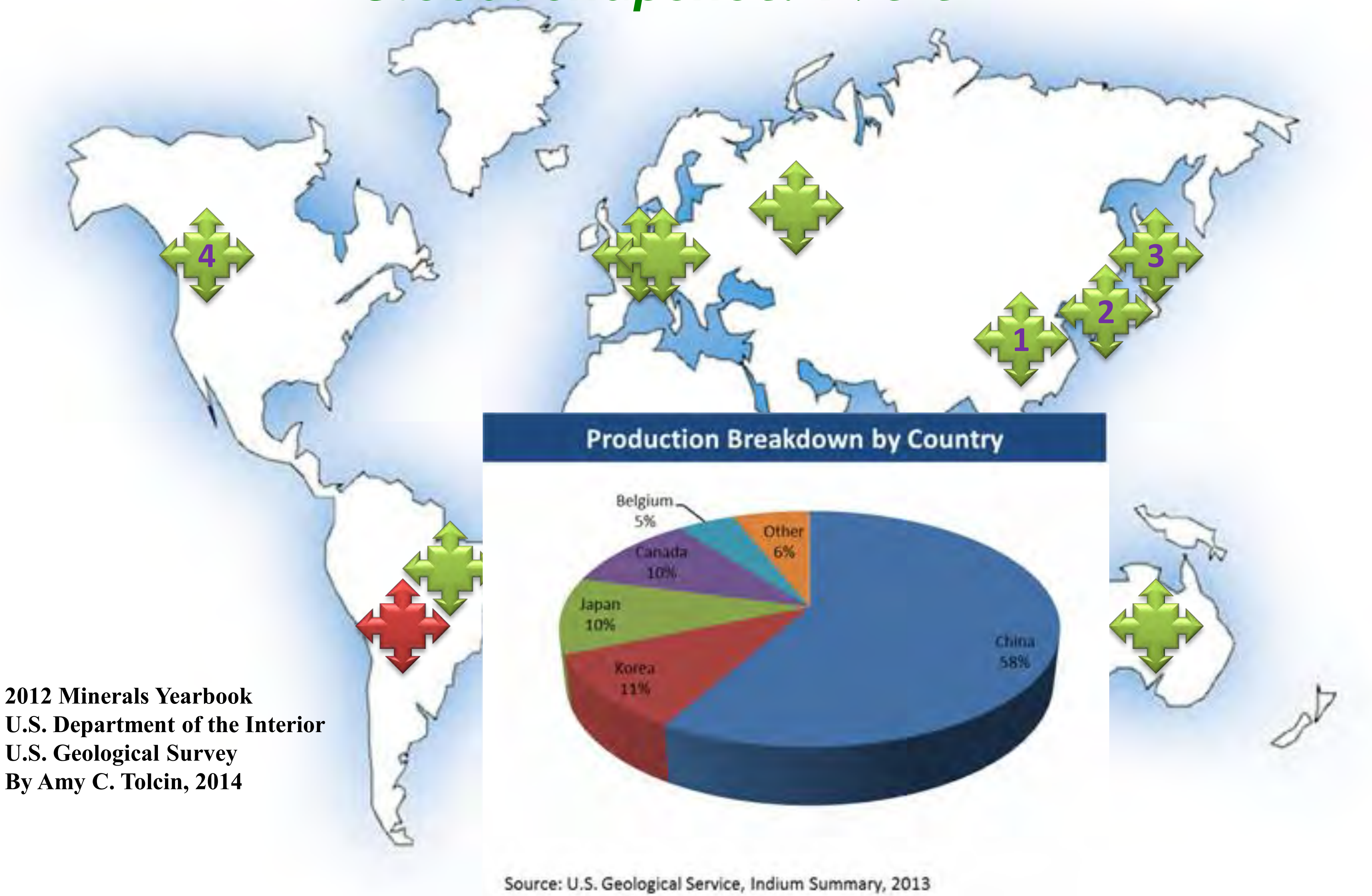
The European Critical Raw Materials review, May 2014



European Perspective
Levels of inter-dependency



Indium – where from?
Global snapshot: 795 t



2012 Minerals Yearbook
U.S. Department of the Interior
U.S. Geological Survey
By Amy C. Tolcin, 2014

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Indium – where from?

A 2012 snap-shot in to USA

2012 Minerals Yearbook
U.S. Department of the Interior
U.S. Geological Survey
By Amy C. Tolcin, 2014

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Audience poll

Which country is the # ONE exporter of indium in to the U.S?

A. China
B S. Korea
C Japan
D Canada

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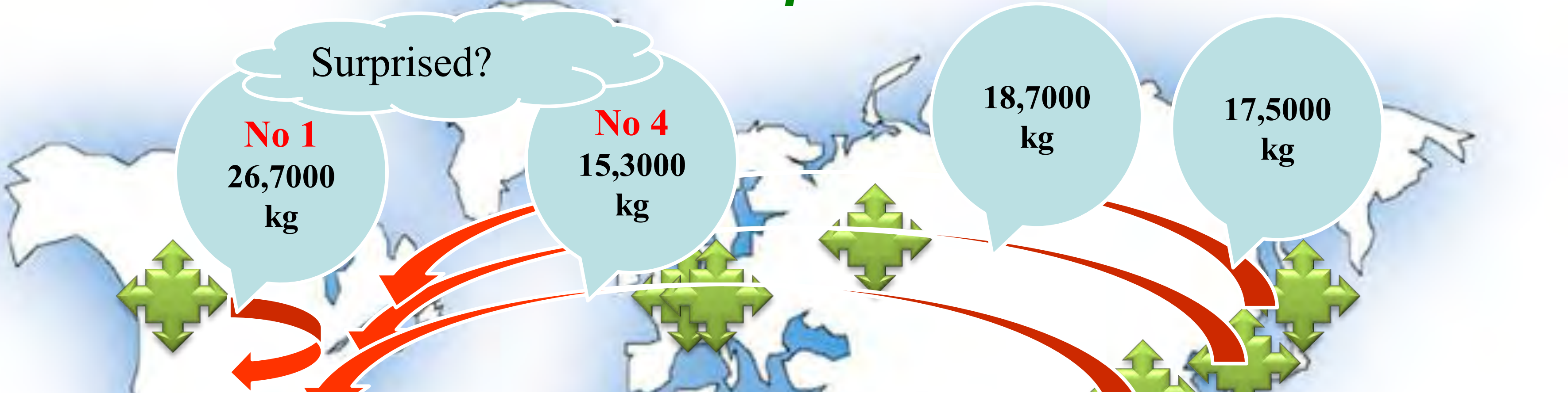
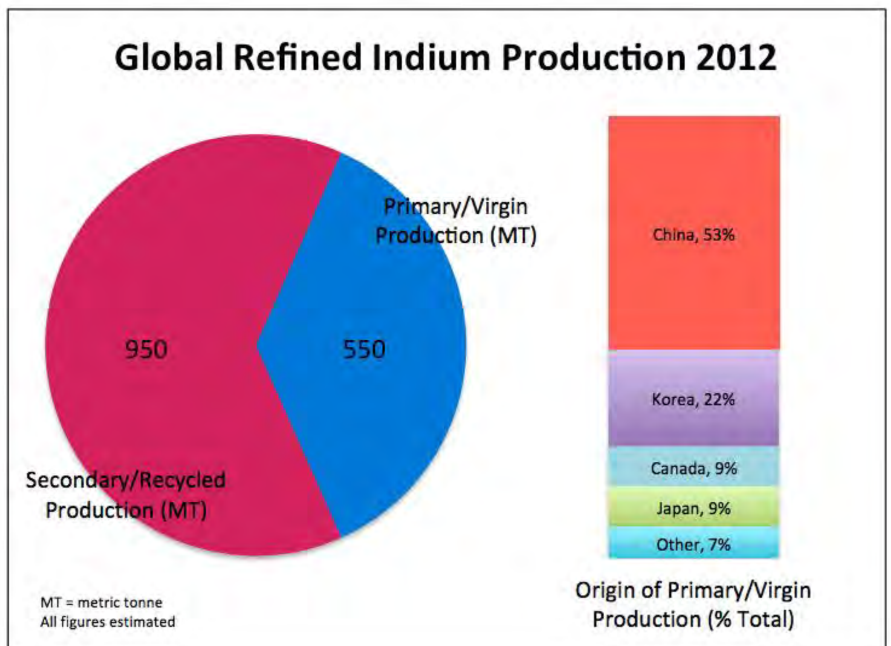
Indium – where from?

A 2012 snap-shot



25% decrease from the 146 t imported in 2011



2012 Minerals Yearbook
U.S. Department of the Interior
U.S. Geological Survey
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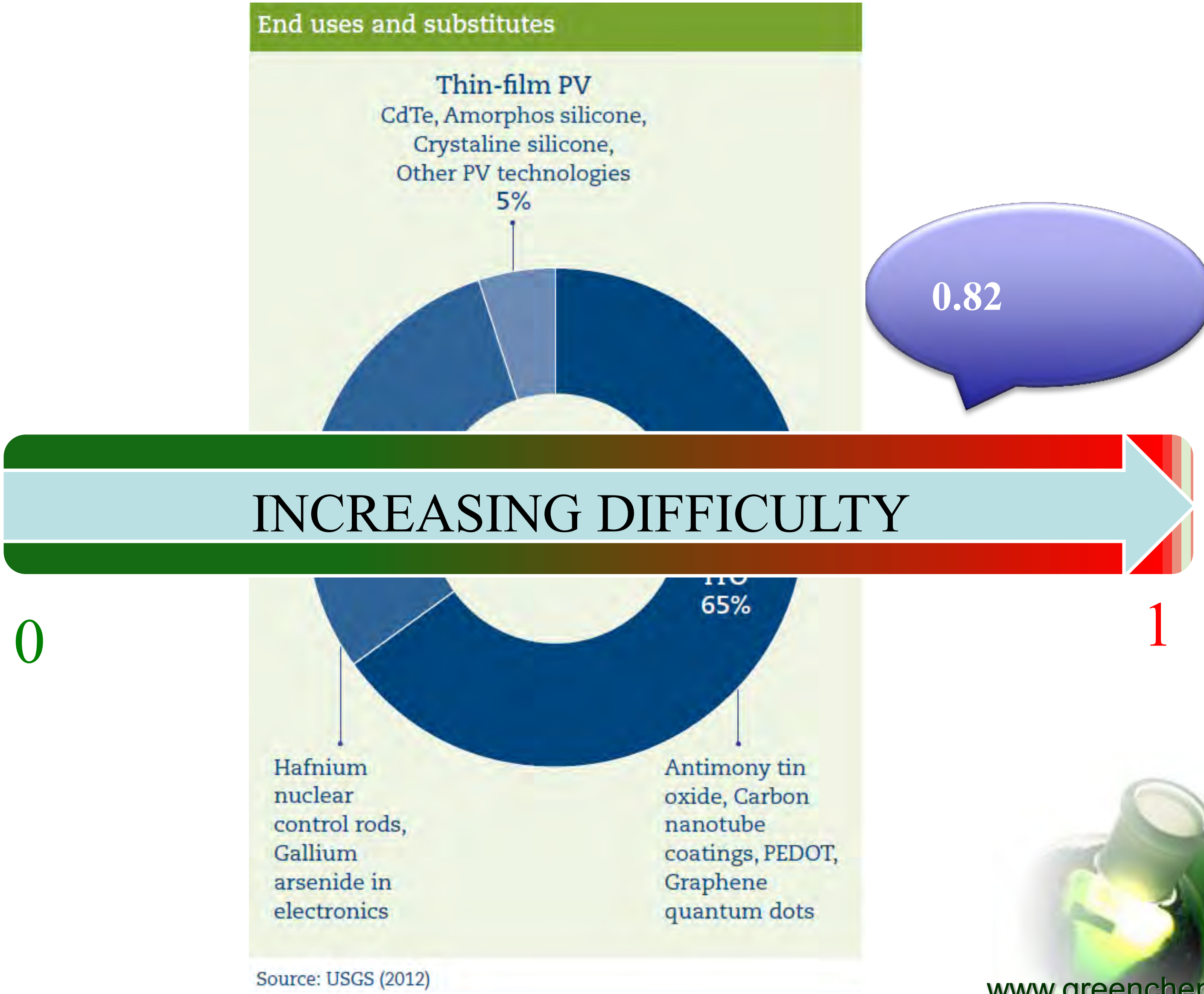
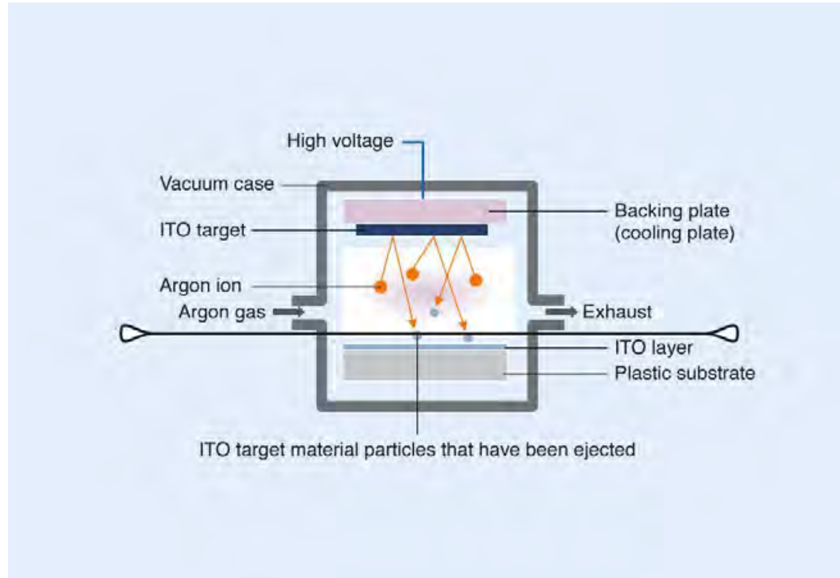
Substitutability Index

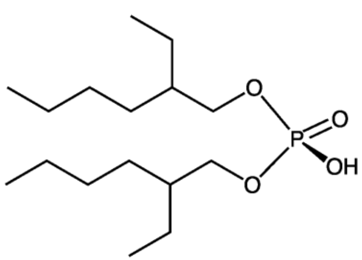


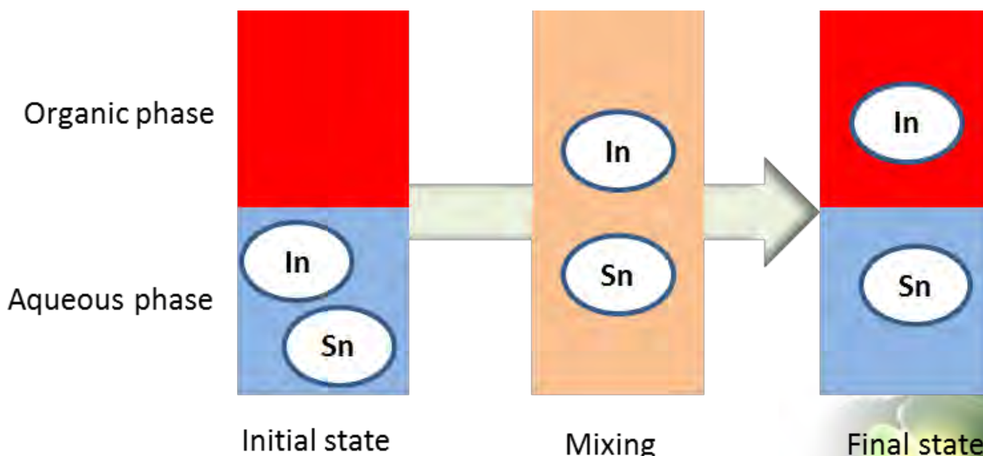
Recovery/Re-use/Recycle

Recovery at source
70% or better



Recovery at EOL
Research stages





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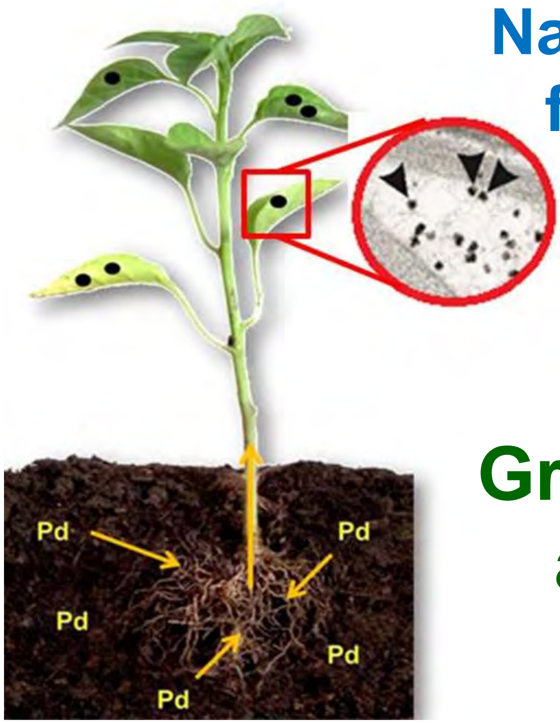
Recovery/Re-use/Recycle

PHYTOCAT
Catalysing the Growth in Metal Recovery

AIM: Capture metals in plants via **phytoremediation** and utilise this trapped metal **insitu** for catalysis, focusing on the platinum group metals.

Waste (mine tailings)

Nanoparticle formation



Metal uptake by plants

Green chemistry applications

A. J. Hunt, C. W. N. Anderson, N. Bruce, A. Muñoz García, T. E. Graedel, M. Hodson, J. A. Meech, N. T. Nassar, H. L. Parker, E. L. Rylott, K. Sotiriou, Q. Zhang and J. H. Clark, Phytoextraction as a tool for green chemistry, Green Process Synth., *2014*, 3, 3–22

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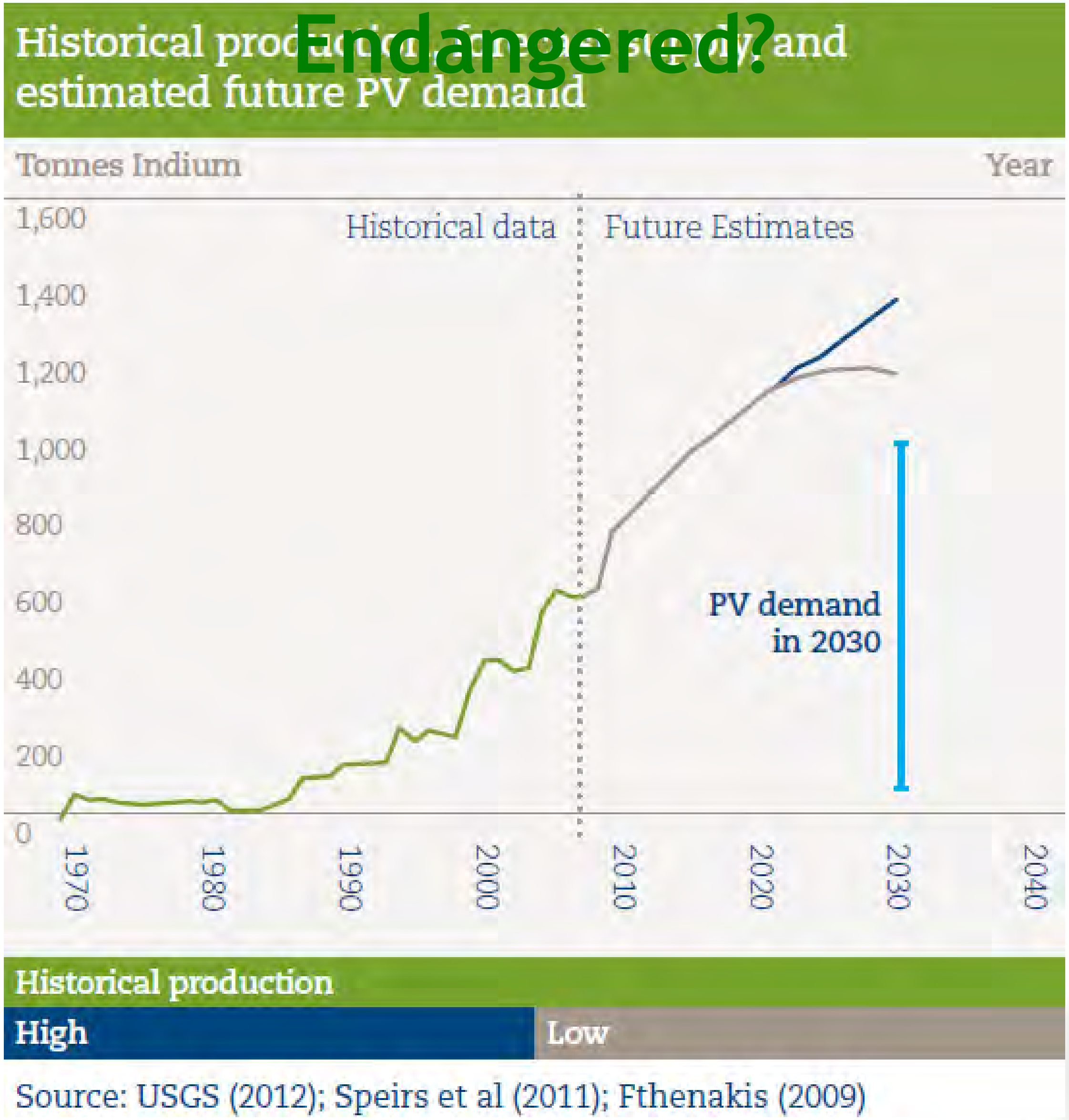
Summary – How Endangered?



UKERC%20Materials%20Handbook_Indium%20(1).pdf

Summary

- Substitution is challenging but represents significant scope for innovation
- Recycling and extraction is limited: uneconomic but may be commercially viable in the long-term
- Need for national and international collaboration
- Who dare estimate ‘global reserves’?
- Stock-piling – some do, some don’t, some did

Summary

- Substitution
- Recycling and extraction is limited:
- Need for national and international collaboration
- Who dare estimate 'global reserves'?
- Stock-piling – some do, some don't, some did

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USGS Mineral Commodity Summaries 2013, Salazar and McNutt, (2013)

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http://www.getfilings.com/sec-filings/130401/SMG-Indium-Resources-Ltd_10-K/

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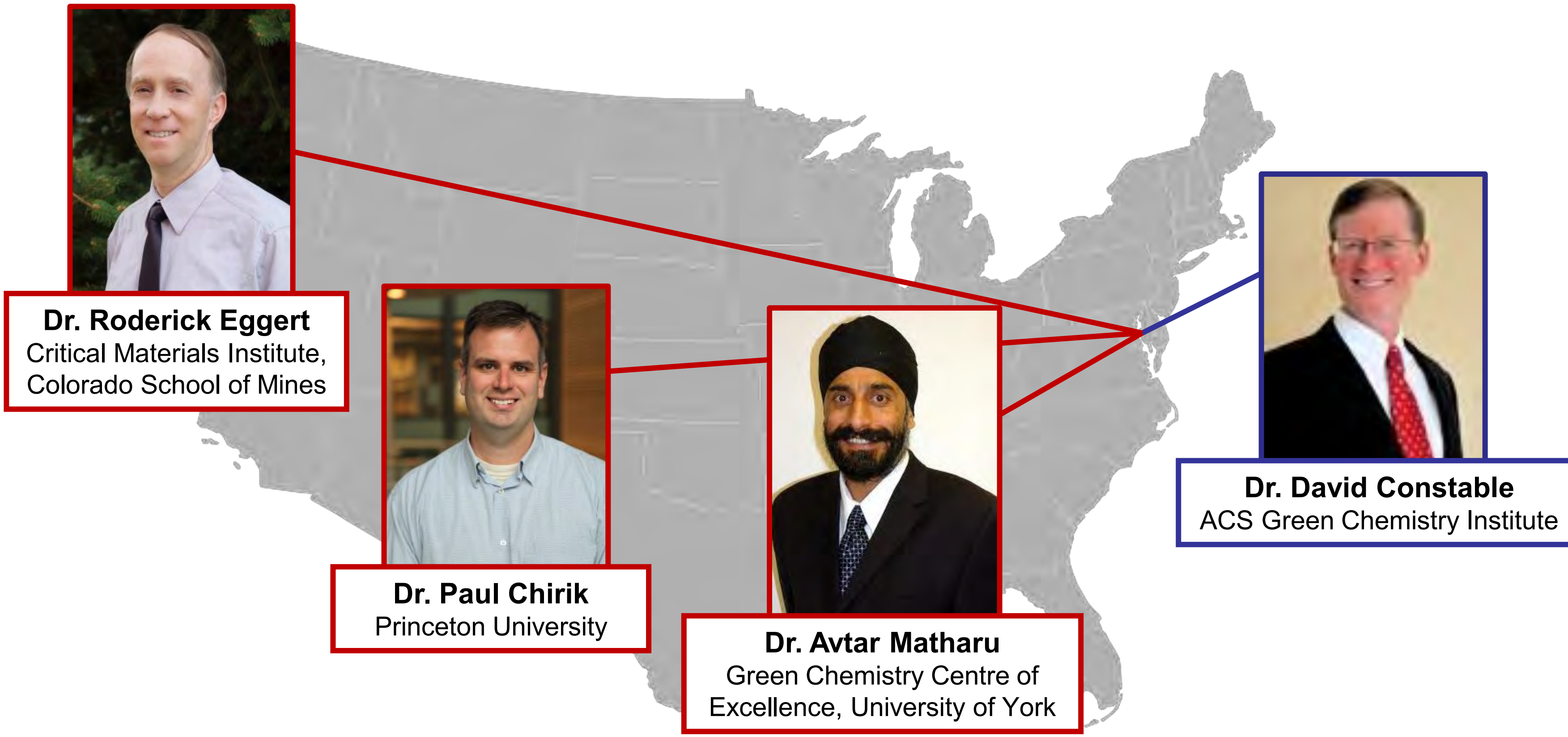
Critical Materials in the Supply Chain



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