Raw Materials Trends -
Impacting the Ceramics and Glass Communities

Dr Mark Patterson

THE UNIVERSITY OF ARIZONA

A statement on the societal changes and the global economy
Will planning and innovation allow us to maintain a competitive position?

Outline

The Earth's resources are fundamental determinants of our "quality of life"

In recent years there has been an increased U.S. dependence on imported commodities that has raised concerns about supply reliability

- Historical perspective, fundamental trends in mineral resource exploitation
- Driving forces affecting current trends
- Supply chain considerations
- Projected changes in the way we address raw materials
- Summary

Quality of Life - Major Influences

- Major conflicts - WWI, WWII, Vietnam and current
- Major inventions -
- Access to space -
- Semiconductors and IC development -
- Mobile devices -
- Light weight materials for transportation -
- Environmental awareness - clean energy technologies
- Sustainable engineering solutions - cradle to grave considerations
- Counter terrorism - better sensors and deterrents
- Robotics and autonomous systems - ???
- Cyber-security - ???
- Healthcare - ???

Source: http://en.wikipedia.org

Certain raw materials have therefore become "key" in maintaining our quality of life
We must ensure that we have the necessary access to these materials or can identify acceptable alternatives

Defining - Strategy for Critical Materials

- Economics - DoC & USGS estimated that the "value added" to the GDP through the use of processed minerals was $2.13 trillion in 2006 (vs. total of $13.2 trillion) and employed 1.5 million people
- Current U.S. population – 11.3 tonnes of minerals per capita to maintain lifestyle

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- Strategic and Critic Materials Stock Piling Act of 1939 and again in 2005 defined materials needed to supply military, industrial and critical civilian needs during times of an emergency
- In 2007 USGS & National Mining Association (NMA) encouraged National Research Council to establish a Committee on Critical Mineral Impacts on the US Economy *"Minerals, Critical Minerals and the US Economy" (2008)*
- In December 2010 Dept. of Energy issued its first "Critical Materials Strategy"
  http://www.energy.gov/news/documents/criticalmaterialsstrategy.pdf
  Strategy focus – "Clean Energy Technologies" - found many at risk to supply disruptions
- In 2010 the American Physical Society (APS) and the Materials Research Society (MRS) jointly published "Energy Critical Elements"

A "strategy" provides a foundation for future action - first step toward a comprehensive response needed to address the challenges before us.

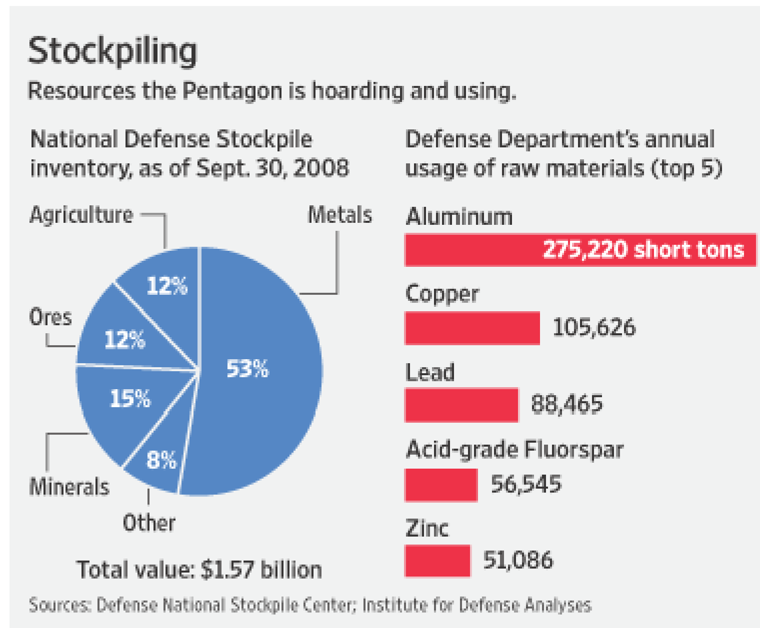
Stockpiling - Strategy for Critical Materials

It is clear that materials play a critical role in defining our quality of life

- 15 materials were stockpiled during WWII
- In 1950 there were 51 materials with a value of $1.6B (with $0.5B on order).
- Korean war this jumped to $8.9B
- In 1962 the stockpile was $7.7B with about 70 materials
- Between 1954 – 1962 sales of the stockpile progressed slowly to sell "excess", and by 1965 about one quarter had been sold off.
- In 1995 - held 90 different <u>commodities</u>;
- In 2008 - held just 20

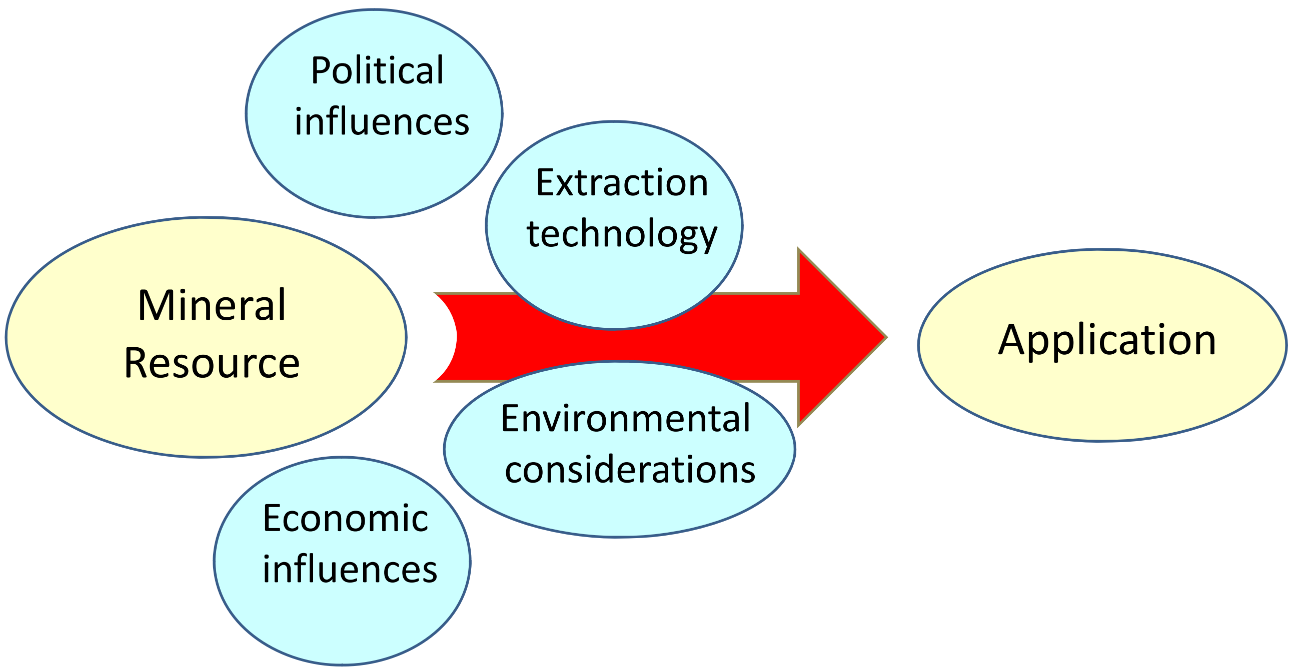
Materials are critical for Defense

- *Defense S&T report (DBS)* 2002 - identified 9 "High Priorities" – materials impacted all
- *Making the Nation Safer*: (NRC) 2002 the role of *Science and Technology in Counter Terrorism* - identified 14 "most important" technical initiatives materials critical for all



Supply Disruption Risks – NAS

- Availability is dynamic – but considered a long term issue
- Reliability – is considered a shorter term issue
- Five, key dimensions are typically considered for primary availability
- Secondary availability (recycling) is an increasingly important consideration



Mineral - Resource Constraints and Pricing

Blackpool Pit, Cornwall (ECLP, now Imery's)

- Kaolin is used in ceramics, paper, paint, plastics, rubber, sealant, adhesives & chemicals
- ECLP was the worlds largest producer of kaolinite in the latter part of the 20th century
- Readily accessible natural resources became more expensive with depth
- Substitution with lower cost fillers (calcium carbonate) – no detrimental effects

Source: http://geograph.org.uk - Jonathan Billinger

War - Political Influences and National "Need"

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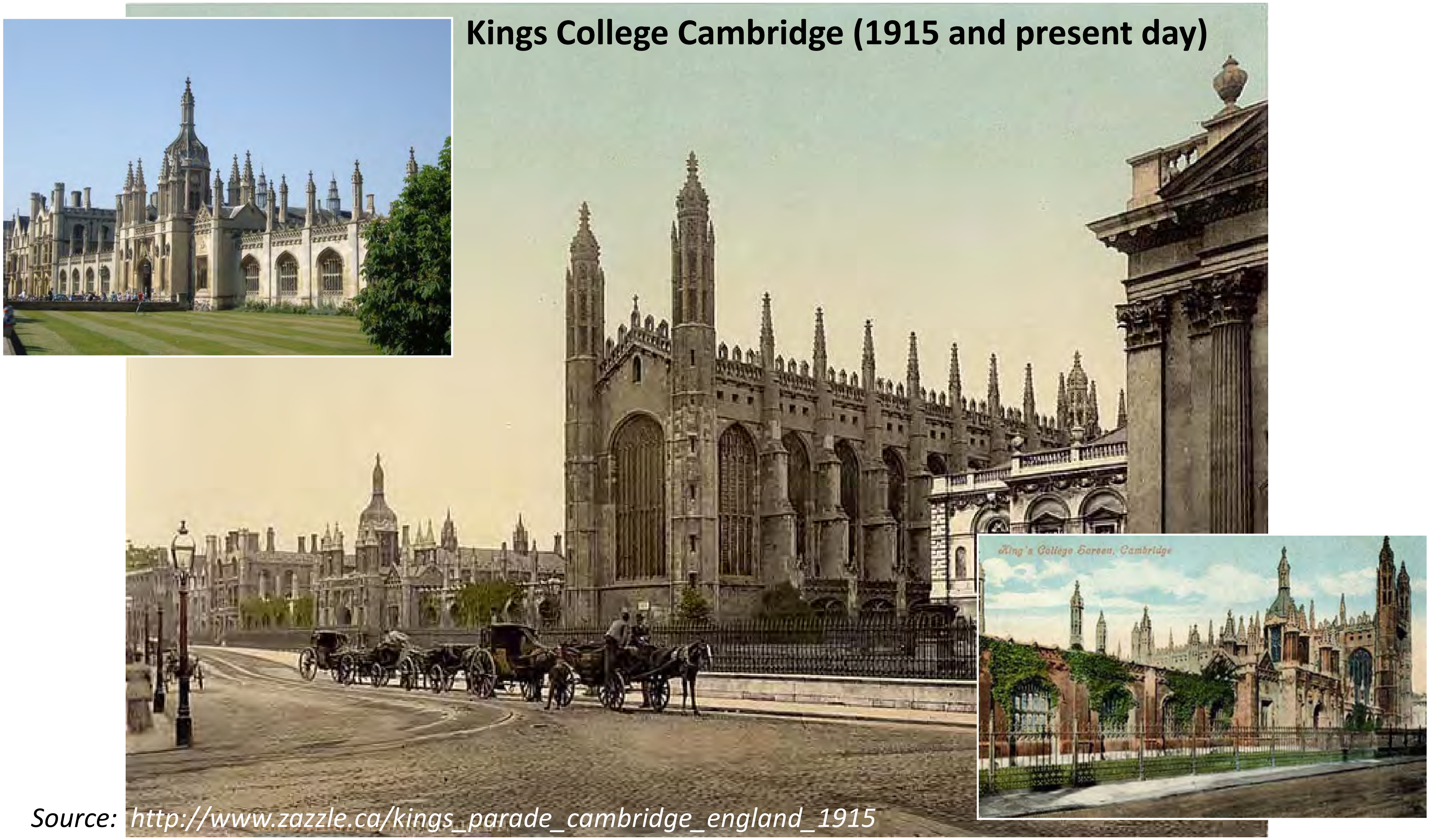
Kings College Cambridge (1915 and present day)



Source: http://www.zazzle.ca/kings_parade_cambridge_england_1915

Extraction - New Processing Routes

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Magnesium

Pidgeon Process (batch)

- High vapor pressure was exploited – batch precipitation of Mg from dolomite

Electrolytic Production

- Step one – generate an anhydrous $MgCl_2$ feedstock
- Electrowinning of anhydrous $MgCl_2$ feedstock

Titanium

Kroll process

- TiO_2 feed concentrate is produced from a few primary ore sources
- TiO_2 is chlorinated to $TiCl_4$ feedstock - purified
- $TiCl_4$ is reduced by magnesium metal - Ti sponge

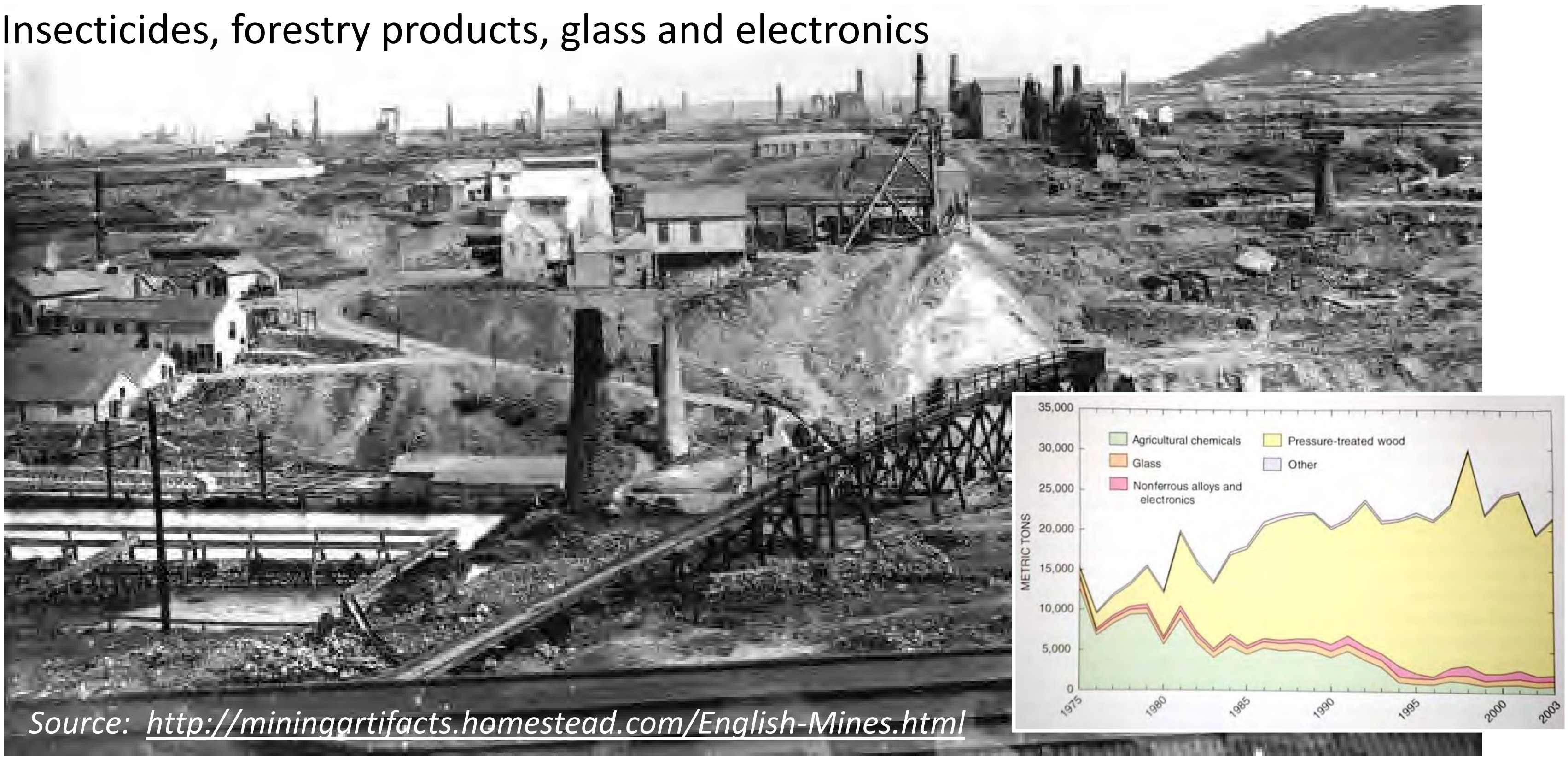
FFC Cambridge process

- Cathode TiO_2 solid pellets and a carbon anode
- Molten $CaCl_2$ electrolyte
- The TiO_2 is sequentially reduced to form Ti sponge directly
- Potential for greater efficiency than with the Kroll process

Environmental - “Life Downstream”

Dolcoath Copper Mine, Cornwall (1799 - 1920)

- Arsenic was produced as a bi-product from Tin and Copper
- Sulphide mineralization, but roasted in “Burning Houses” to As_2O_3
- Latter part of the 19^{th} century, Cornwall led the world in Arsenic production
- Insecticides, forestry products, glass and electronics



Source: http://miningartifacts.homestead.com/English-Mines.html

Economic - Pricing Fluctuations

Rare Earths

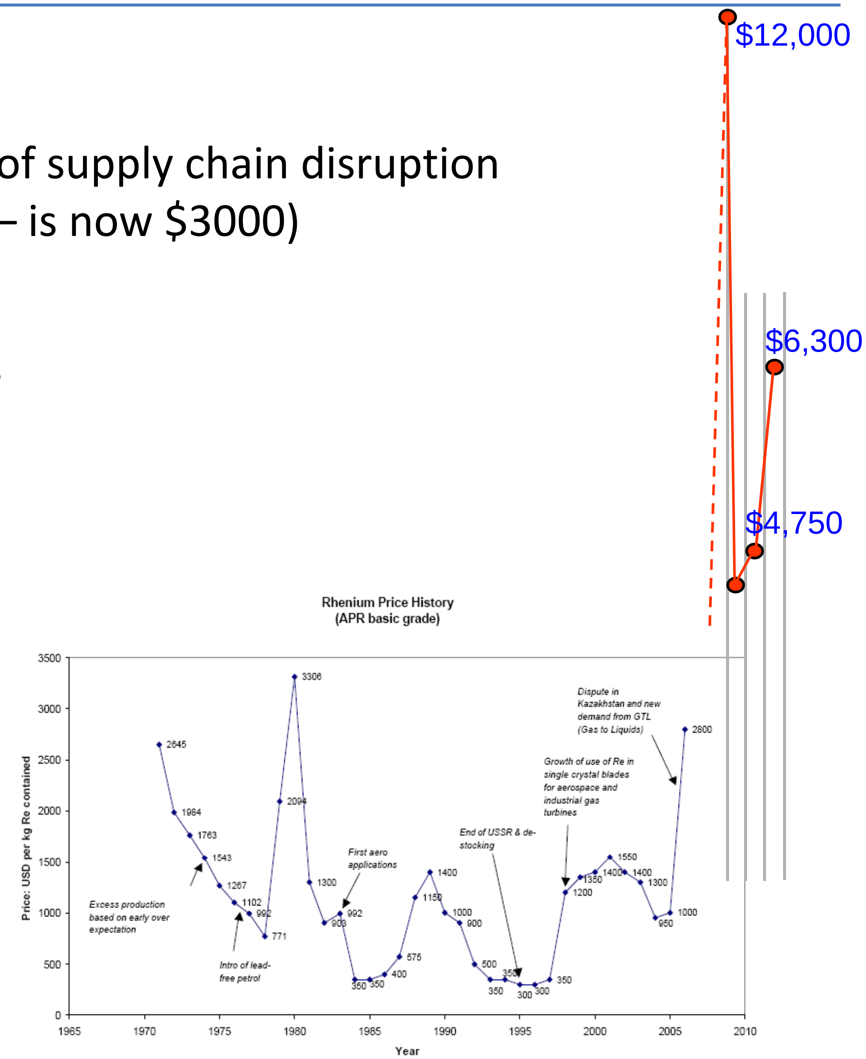
Rare Earths have been in the public news – fears of supply chain disruption
Dysprosium $300 (hybrid cars and smart phones – is now $3000)
Nd also rose from $45/kg to $450 current price.

Global demand for TREO is about 130,000 tonnes

Rhenium

"It is a sad fact that until the value of Rhenium reaches a level where it is fully seen on the radar of those who need it, important quantities will continue to be lost". Source: 2008 Anthony Lipmann (Minor Metals Trade Assoc.)

Global production for Re is only 40 tonnes



National Academy of Sciences - Overview

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NRC Study Objectives

- To determine which minerals could be considered “critical” to the Nation
- To identify additional information and research that might help mitigate disruptive fluctuations in the supply of critical minerals to key economic sectors

Summary of major findings

- The US is both a major supplier and user and could not function without critical minerals and the products made from them.
- The federal government should lead a coordinated effort in researching and collecting information on minerals and metals
- The federal government has a responsibility to conduct and support research and to gather and disseminate information on minerals and metals
- The federal government should help facilitate activities (exploration, development, technology, recycling, environmental protection) that sustain mineral supplies
- The federal government should maintain core competence in;
    - The knowledge of mineral deposits
    - Related environmental research
    - Extraction techniques and implications
    - To respond to future national needs
- Globalization - mineral resources have become an issue for National Security

“Critical” Materials Considerations (NAS)

A “critical mineral” is both essential in use **and** subject to the risk of supply restrictions
The criticality of a certain mineral is likely to change as technologies evolve
When considering “criticality” of minerals it is important to distinguish between short, medium and long time frames

Short and medium terms

- Significant increase in demand
- Thin markets
- Concentration of production
- Production predominantly as a bi-product
- Lack of availability of old scrap or infrastructure for recycling

Long term

- Function of investment
- Geological allocation

Public and private decision makers need access to unbiased mineral information
There needs to be a mechanism to collect and disseminate critical minerals information

Materials Evaluated – NAS Selections

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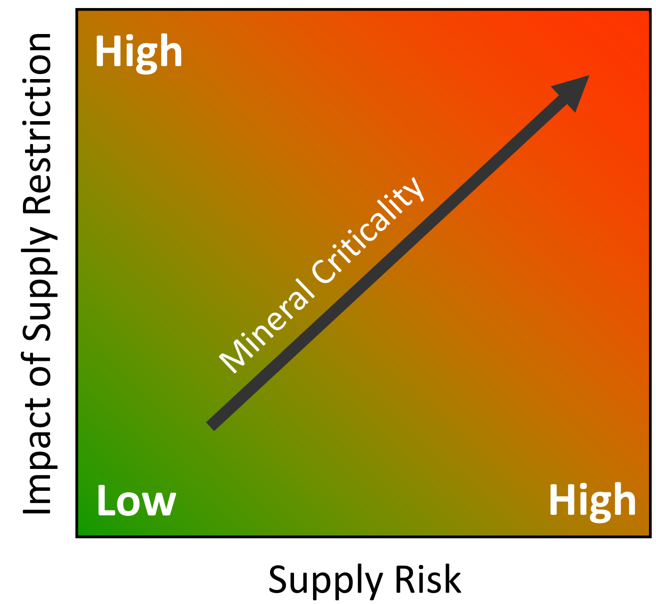
- The committee concluded that all minerals could become critical to some degree
- The following minerals were however investigated

Copper, Gallium, Indium, Lithium, Manganese
Niobium, PGMs, Rare Earths, Tantalum, Titanium
and Vanadium

- The committee concluded that from the federal gov. perspective – should be “essential” in use and subject to supply restrictions
- The following minerals were determined “critical” because of application, difficulty of replacement and risk of supply

Platinum Group Metals, Rare Earths, Indium
Manganese and Niobium

Geologic
Technical
Environmental and societal acceptance
Political and
Economical

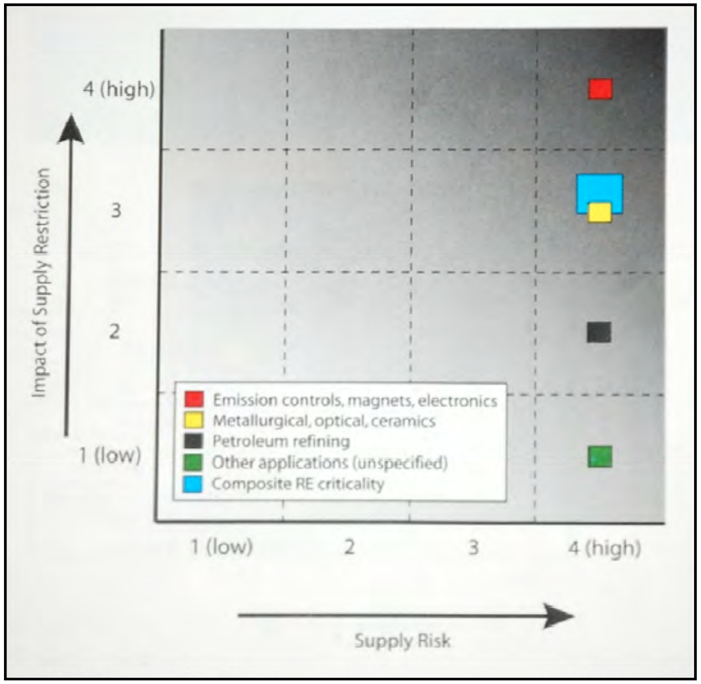


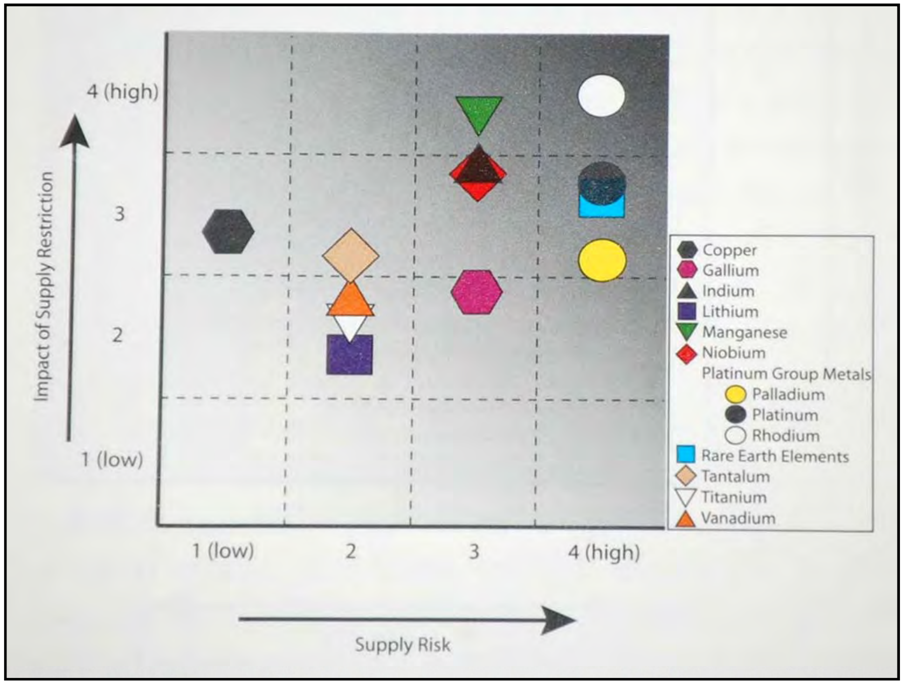
The Criticality Matrix

Materials Evaluated – NAS Selections

- Criticality assessment for Rare Earths
  - The use of Rare Earth Minerals in various end use applications shows how the criticality based on industry sector/application
- Criticality matrix for each of the 11 minerals assessed.
  - This matrix identifies indium, manganese, niobium, PMGs and REs as falling within the "critical" zone

Source: Minerals, Critical Minerals and the US Economy NRC 2008





Department of Energy Study - Overview

It is projected that Renewable Energy and Energy Efficient technologies with grow substantially in future years – many applications rely on "critical" materials

Objective of the current study

- Assess risk and opportunities in the area of energy technologies
- Inform the public and establish a dialogue
- Identify possible programs and policy directions

Studied components used in Clean Energy Technologies

- Permanent magnets (*wind generation and electric vehicles*)
- Advanced batteries (electric vehicles)
- Thin-film semiconductors (*photovoltaic power systems*)
- Phosphors (*used in high efficiency lighting systems*)

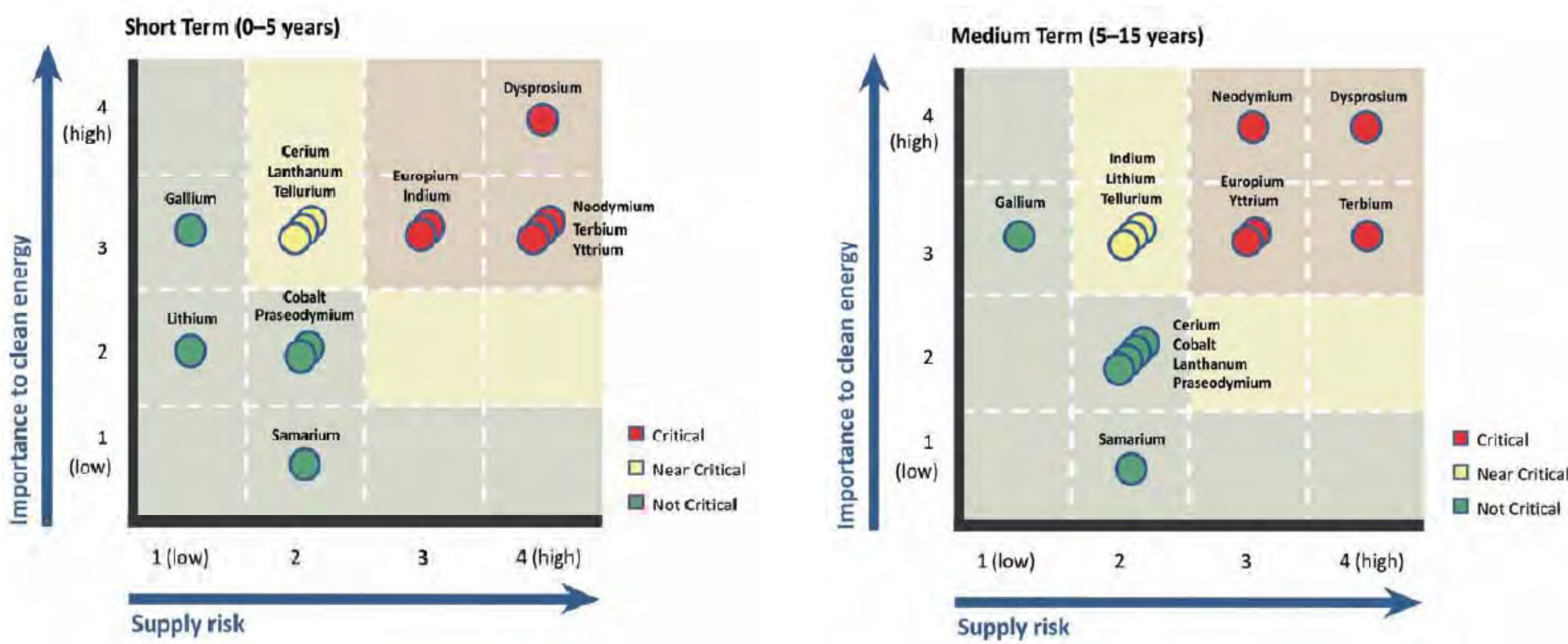
Criticality assessment

- Terbium, neodymium, dysprosium, yttrium, europium and indium all appear critical short term (0 to 5 years)
- With the exception of Indium, materials remain critical in the (5 to 15 year) term

Materials Evaluated – DoE Selections

- The strategy adopted by DoE rests on three pillars
  - Diversified global supply chains are necessary with multiple sources of materials
  - Substitutes must be developed – improve flexibility and meet clean energy needs
  - Recycling, reuse and more efficient use will significantly reduce world demand

Lanthanum, Praseodymium, Neodymium, Yttrium, Lithium, Tellurium, Cerium, Gallium, Indium, Cobalt, Samarium, Europium, Terbium and Dysprosium



Source: http://www.energy.gov/news/documents/criticalmaterialsstrategy.pdf

NAS - US Key Market Sectors Evaluated

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- Most important sectors of the economy for mineral use are;
  - Transportation, including automobiles and aircraft
  - Capital equipment such as industrial machinery
  - Residential and commercial construction
  - Consumer durables – washing machines, refrigerators, cell phones and televisions
- Defense is a special sector;
  - NRC Committee on Assessing the Need for a Defense Stockpile (2007)

- Overview for the following market sectors;
  - Automotive
  - Aerospace
  - Electronics
  - Energy
  - Others

Automotive - Overview

Early Automobiles

- Contained a very small suite of materials;
  - Steel, wood, rubber, glass and brass (Vanadium steel alloys – first improvements)

Modern Automobiles

- Modern vehicles contain in excess of 39 elements from primary minerals
- Improved strength at reduced weight led to various steel alloys – Mo, Cr, Ni, Mn, with V
  - Mo, imparts improved strength and toughness to stainless steels
  - Late 1970's saw a sharp increase in the price of Mo – development of HSLA steels;
  - Cr gave higher corrosion resistance and hardness
  - Ni gave better HT strength and Mn alloyed with Al and Cu to give harder steels
- Al competes with steel for high strength, light-weight, corrosion resistant alloys
- Recent Hybrid designs have increased Cu from 50 lbs to 75 lbs, and more Co, Ni and Li
- PGMs are used in the catalytic converters
  - Pt reduces CO and HCs (Pd can replace Pt in gasoline engines – but not diesel engines)
  - Rh reduces NOx emissions and is unique
- Rare Earths are critical in the operation of modern cars (46% of US use in 2007)
  - Ce and La are critical in the operation of catalytic converters
  - Nd is critical in high strength magnets

Aerospace - Overview

Critical sector for US export revenues

- In 2006;
  - Exported $28B in aircraft and $16B in jet engines

Three primary systems to consider

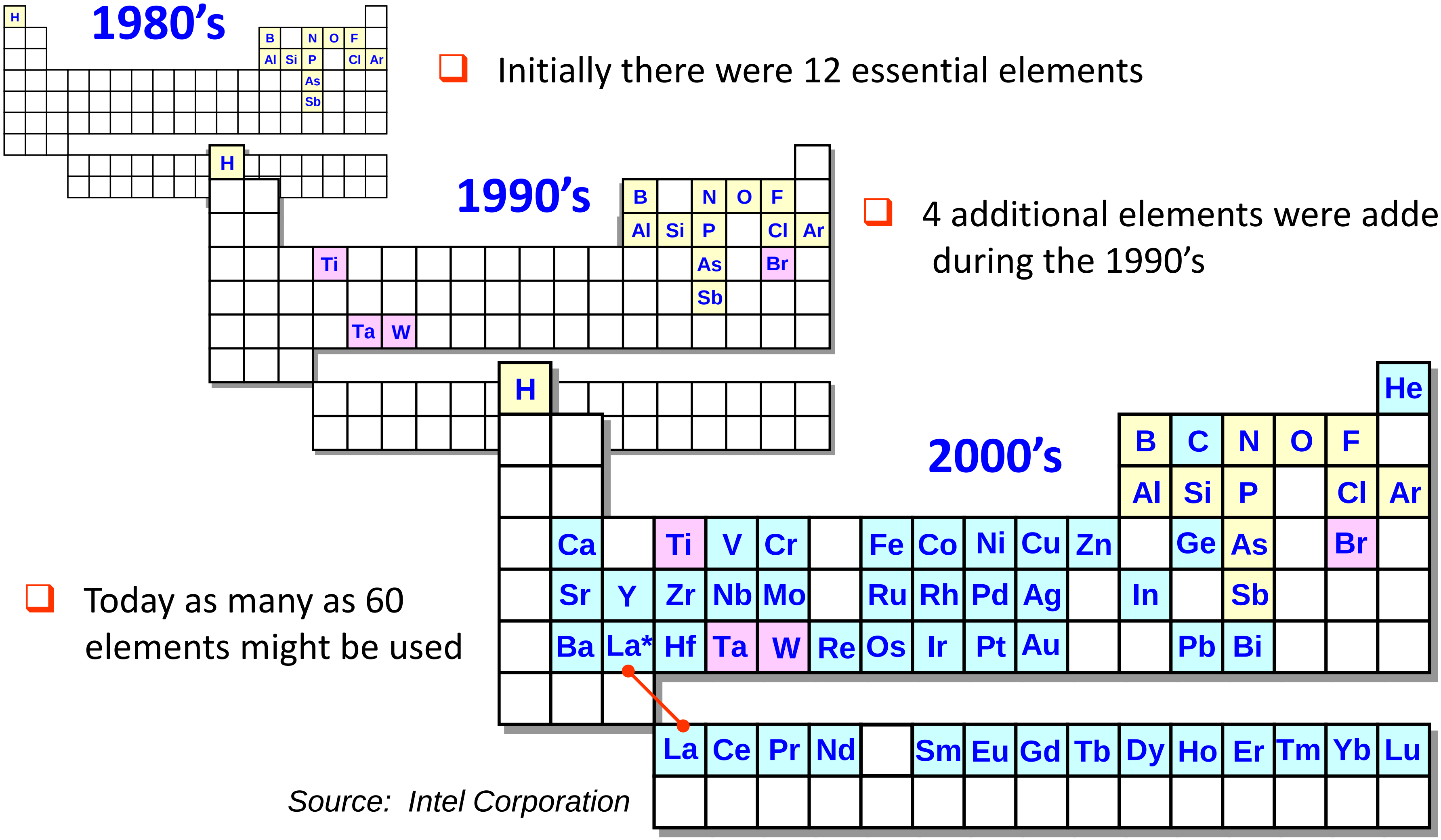
- Propulsion – thrust to weight improved from 1941 (1.5:1) to 2007 (6.8:1)
  - Ni and Co based super-alloys improved high temperature strength
    - Additions of Al and Ti - precipitates;
  - Ti based super-alloys
    - Reduced the overall weight but relied on expensive, foreign Ti sources
  - Introduction of thermal barrier coatings based on YSZ
- Structure - cloth, metal, composites
  - Higher strengths have been achieved with MMCs and PMCs (fiber reinforced)
  - CNT reinforced structures are likely to find structural applications – strike protection
- Avionics - Electronics, computing, radar and other sensors
  - Benefited from the very rapid growth in the electronics sectors
  - Increased autonomy, self awareness and computing
  - Improvements to the user interface

Electronics - Overview

The electronic sector is dynamic and growing rapidly, driven in part by the desire to miniaturize, improve energy efficiency and increase performance (processing speed)

- Computing, communications, entertainment, energy management, sensing etc.,
- Relies on the properties of elements derived from around 60 minerals
- Specific performances are achieved from unique combinations of materials;
- Possessing unique electrical, dielectric or optical properties – atomic structure
  - $Ba_3ZnTa_2O_9$ - resonator for cellular telephone base stations
  - InGaAs - semi-conductor
  - HfO_2 - high dielectric constant film on Si for micro-electronic chips
  - Inexhaustible and growing list
- Liquid crystal displays – $InSnO_2$ with a broad range of configurations and additives
- Computer chip manufacturing……..

Computer Chip Technology - Evolution



- Initially there were 12 essential elements
- 4 additional elements were added during the 1990's
- Today as many as 60 elements might be used

Source: Intel Corporation

Energy – PV Clean Energy

Receiving considerable attention due to rising fuel costs, the impacts of climate change and avoiding generating greenhouse gases

- Photo-voltaic devices– low environmental impact and low operating costs
  - Silicon wafers, CdTe, Cu(In,Ga)Se_2 thin films
  - High purity Si production is slated to increase significantly
  - Major initiative to produce cells for $1/watt – NY State

- Projected that PV may produce half of "new" U.S. electricity by 2025

Solar Power Systems (GW)	2004	2015	2030
Annual U.S. Shipments	0.12	2.3	19
Cumulative U.S. Installations	0.34	9.6	200
Source: Solar Energy Industries Association 2004			

- Price volatility for In and Te may impede more wide-spread adoption for thin film PVs

Energy – CdTe and Next Generation PV Devices

- Supply chain for CdTe
  - Globally well distributed
  - Extracted as secondary, from copper anode slimes
  - Purification of materials – takes place in Canada
  - Cells, modules and systems are typically made in Asia
    - lower labor costs, favorable policies to manufacturing

Reducing costs while maintaining a diversity of manufacturing technology options is preferable – reduces sole source dependency. Recent interest with increasing US production and alternative technologies

- Next generation solar cells
  - Organic and dye sensitive solar cells
  - Researchers have consciously focused on lower cost readily available materials
  - Potential formulations are based on FeS_2, CuS_2 and Zn_3P_2

Energy - Batteries

- Batteries – Ubiquitous mobile power sources;
  personal appliances, computers, motor vehicles, aerospace, military and others
- Li-ion and Ni-metal hydride - rechargeable, long life cycle, high energy density
  - Recycling of Li batteries primarily addresses improper disposal
  - Recycling however, is considered important with regards to supply outlook
- Ni-metal hydride are more common but contain REs in the anode
  - (approximately 20kg of REs are estimated for electric cars)
- Ni-Cd batteries are now largely replaced by Li batteries for portable
  - devices due to power density and weight
- Disposal of Lead-acid or Ni-Cd batteries – usually results in handling more toxic
  - materials than would be the case with Li-ion or Ni-metal hydride batteries

Energy – Phosphors and Lighting

- Phosphors and Lighting – Accounts for 18% of electrical use in US;
- 7% of all Rare Earth use and 32% of the total Rare earth revenues
- Four main areas of interest
  - Traditional incandescent
  - Fluorescent
  - Light emitting diodes
  - Organic light emitting diodes

- Fluorescent lamps are either linear or compact
  - Lanthanum and Terbium phosphors
- Light emitting diodes
  - Ce & Eu phosphors, Ga & In semiconductors Nd as glass additives

In the short term the demand for Rare earths in LFL and CFL phosphors is expected to grow to 230% of current levels. In the long term, LEDs and OLEDs may take over eliminating the need for rare earth phosphors

Minerals in Decline

- Changes in technology, lower price substitutes, concerns regarding health and safety and government regulations - significant decline in As, Hg and Pb

- Arsenic - still used in electronics, non-ferrous alloys and glasses
  - concerns with As entering into the ground water
- Lead - at one time used in gasoline (1995), paints and pigments (1977)
  - currently under considerable pressure to be removed from solders (difficult)
  - lead continues to be used in Pb-acid batteries (only because of recycling)
- Mercury - alkaline primary batteries (1989)
  - still being manufactured in fluorescent lamps.
  - amounts are small but collectively create a problem

Minerals on the Increase

- Changes in technology, lower price substitutes, concerns regarding health and safety and government regulations - increase the use of Ga, Ge, In, and Sr

- Gallium - growing use in integrated circuits. LEDs, photo-detectors and solar cells
  - GaAs has semiconducting properties
- Germanium - growing use due to semiconducting properties in electronics
  - optical glass fiber properties
  - chemotherapy - treatment of some forms of cancer
  - small production in US (Belgium, China and Russia) 25% from recycling
- Indium - LCDs as ITO
  - all Indium in the US is imported

Recommendations – energy critical materials

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- General consensus - supply risks and uncertainties for many "critical" materials
  - Rare earths (Neodymium, Yttrium, Indium, Europium, Terbium and Dysprosium)
  - Indium specifically, is considered a short term concern
  - Rhenium – possible replacement with Hf or Ta compounds
  - PGMs – unique catalytic properties supporting broad technologies
- Coordination - OSTP should create a subcommittee within NSTC – federal response
- Information - US government should set up a "Principal Statistical Agency" tasked with monitoring the use of energy critical materials, supply chain, disposal, recycling and emerging energy technologies to identify critical applications and potential shortfalls
- Research and Development - Federal government should coordinate and fund research focused on energy critical elements and substitutes. This should encompass deposit modeling, extraction, processing, characterization and life cycle analysis
- Materials efficiency - Establish a consumer oriented "critical materials" designation for energy related products
- Market Intervention - A non-defense-related economic stockpile of critical energy related materials is not recommended – with the exception of Helium.

Rare Earths - Recent Actions……..

Rare Earths – globally distributed although concentration varies
Exploration of alternative domestic sources of Rare Earths (primary and secondary)
Invest in R&D, substitutes, recycling, re-educate work force now

- Avalon, - Nechalacho Deposit, Thor Lake, NWT, is emerging as one of the largest undeveloped rare earth elements resources in the world. At 1.53% TREO and 0.33% HREO
- Frontier - Zandkopsdrift Rare Earth Element Project in South Africa again claim to be the largest outside of Chinese and Molycorp grade 1.9% to 2.3% with HREO
- Japan – 100 billion tonnes (one fifth the worlds) at the bottom of the ocean in mud. They have invested $1B in securing a future with $300 - $400M in resources
- N.America – 900 new projects for domestic sites - new mines cannot come on-line quickly, but also the main problem is in producing the RE oxides
- Current global demand for TREO is about 130,000 tonnes
- NSF and DoE will collaborate on strategic materials – 2 cosponsored ERC grants
- US government needs to step in and secure US resources before they are purchased by foreign interests. $20B investment is necessary for a 10,000 tonne, 10 year resource
- Study needs to be expanded to include U and coal. - China has 220 C plants ($2.27/MBTU)
- US – Russia agreement on Uranium ends in 2013. 10% of all light-bulbs are lit by down-blended U and so there will likely be a spike in the cost at that time

Alternatives

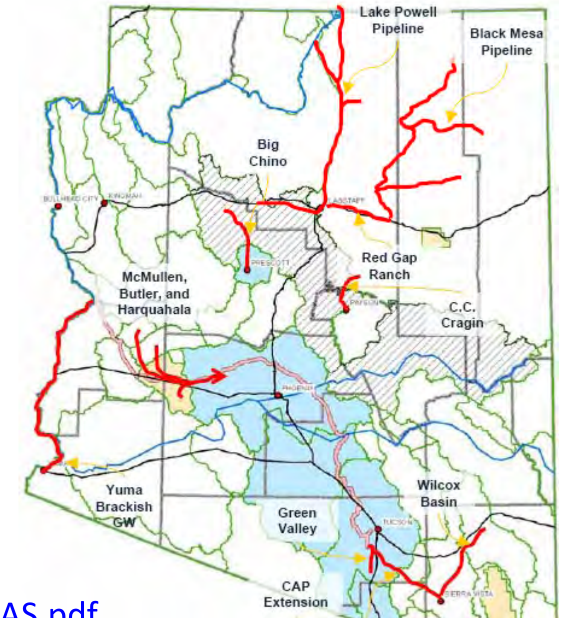
- Substitutes for ITO have been evaluated – Antimony TO has been ink jet printed onto LCDs coatings and successfully annealed onto LCD Glass
- Poly(3,4-ethylene dioxythiophene) (PEDOT) can be spin coated
- Graphene quantum dots have also been developed to replace ITO electrodes
- More adhesive ZnO nano-powders have been developed to replace ITO in LCDs
- In Phosphide can be substituted by gallium arsenide in solar cells and other applications
- Hf may replace In (and Ag-In-Cd) in Nuclear reactor control rods

  - Iodine based solutions have replaced Cyanide for gold and U complexes
  - Mining selectivity, for in-situ applications
  - Improved resource characterization
  - Bioluminescent illumination

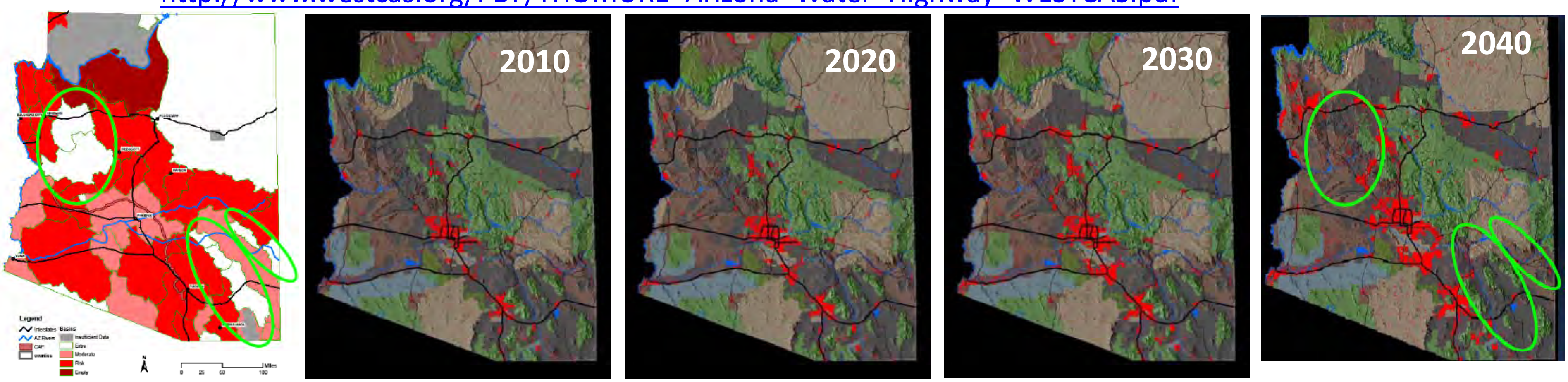
Water - Arizona

- Population is projected to grow from 6M to 12.8M by 2050
- Municipal water demand to increase by 110%
- Proposed Ground Water Transfers for 2040
  - Red Gap Ranch
  - Big Chino
  - McMullen, Butler, and Harquahala
  - Black Mesa
  - Brackish Supplies

Water management will be critical for nearly all industries



Source: http://www.mag.maricopa.gov/
http://www.westcas.org/PDF/THOMURE_Arizona_Water_Highway_WESTCAS.pdf



Summary

- Our "quality of life" is dependant on several critical/strategic raw materials
  - Many of these depend upon the specific electronic, optical or physical properties of specific elements or combination of elements
  - Certain rare earths, PGM, Re and Indium are critical in the short term and certain rare earths currently remain critical in the longer term (5 – 15 years)
- Reducing costs while maintaining a diversity of manufacturing technology options is important
- To respond to future national needs it's suggested;
  - Maintain core competencies in
  - The knowledge of mineral deposits
  - Related environmental research
  - Extraction techniques and implications
- With globalization – mineral resources have become an issue for National Security
  - Government leadership and support is important
- Technology is advancing quickly and innovation through R&D remains key
  - Once problems become sufficiently "painful" - innovative solutions can be sought – but only if they are identified in sufficient time……..
- With innovation comes a "new" set of issues and considerations