

Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues

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Presentation Outline

- Introduction to the Rare Earth Elements
- Why are we interested in them and where are they found in the US?
- How are they acquired and what are potential environmental impacts?
- What are the emerging policies and alternatives to REEs?
- ORD NRMRL ETSC Technical Support Publication Document
- Key Findings and Next Steps of the Document
- Where to go for more information

Introduction to the Rare Earth Elements



Powders of six rare earth elements oxides. Photograph by Peggy Greb, Agricultural Research Center of United States Department of Agriculture.

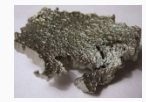
- 15 lanthanides
- La through Lu
 - Pm is rare in nature – mostly human-made
- Plus scandium and yttrium are often included
- a.k.a. Rare Earth Minerals, Oxides, and/or Metals

Introduction to the Rare Earth Elements

1 H Hydrogen 1.00794																	2 He Helium 4.003																												
3 Li Lithium 6.941	4 Be Beryllium 9.012182															5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.006434	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797																								
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050															13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.0666	17 Cl Chlorine 35.4527	18 Ar Argon 39.948																								
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80																												
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29																												
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	58 Ce Cerium 140.12	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93040	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967																													
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)																																		
<table border="1"> <tr> <td>58 Ce Cerium 140.116</td> <td>59 Pr Praseodymium 140.90768</td> <td>60 Nd Neodymium 144.24</td> <td>61 Pm Promethium (145)</td> <td>62 Sm Samarium 150.36</td> <td>63 Eu Europium 151.964</td> <td>64 Gd Gadolinium 157.25</td> <td>65 Tb Terbium 158.92534</td> <td>66 Dy Dysprosium 162.50</td> <td>67 Ho Holmium 164.93032</td> <td>68 Er Erbium 167.26</td> <td>69 Tm Thulium 168.93040</td> <td>70 Yb Ytterbium 173.054</td> <td>71 Lu Lutetium 174.967</td> </tr> <tr> <td>90 Th Thorium 232.0381</td> <td>91 Pa Protactinium 231.03888</td> <td>92 U Uranium 238.0289</td> <td>93 Np Neptunium (237)</td> <td>94 Pu Plutonium (244)</td> <td>95 Am Americium (243)</td> <td>96 Cm Curium (247)</td> <td>97 Bk Berkelium (247)</td> <td>98 Cf Californium (251)</td> <td>99 Es Einsteinium (252)</td> <td>100 Fm Fermium (257)</td> <td>101 Md Mendelevium (258)</td> <td>102 No Nobelium (259)</td> <td>103 Lr Lawrencium (262)</td> </tr> </table>																		58 Ce Cerium 140.116	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93040	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967	90 Th Thorium 232.0381	91 Pa Protactinium 231.03888	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)
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Wikipedia photo = Assortment of lanthanoide group elements. Uploaded at 22:12,19 April 2006 by [User:Tomihhndorf](#). Author [User:Tomihahndorf](#). Permission=GFDL.



Scandium



Yttrium

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Periodic table of the elements showing the division between LREEs and HREEs (Schuler et al., 2011).



Introduction to the Rare Earth Elements

- Similar chemical properties
 - Electropositive (valence 3+) – Ce^{4+} and Eu^{2+} also in natural systems
 - Differ from other metals (Valence located in inner 4f subshell orbital, shielded by 5s² and 5p⁶ outer closed (full) subshells)
 - Stable outer shell results in very similar chemical properties and difficulty in their separation during processing
 - Atomic nucleus is poorly shielded and with increasing atomic number, 4f shell electrons pulled closer to the nucleus
 - Reduction in the ionic radii with increasing ionic charge
 - Lanthanide Contraction
- Not really rare – term stems from 1940's/50's
- Don't occur as native elemental materials
 - Host mineral's chemistry
 - Bastnasite, Monazite, Xenotime, and others



Introduction to the Rare Earth Elements

Abundance of Elements in the Earth's Crust

Elements	Crustal Abundance (parts per million)
Nickel ($_{28}\text{Ni}$)	90
Zinc ($_{30}\text{Zn}$)	79
Copper ($_{29}\text{Cu}$)	68
Cerium ($_{58}\text{Ce}$)^a	60.0
Lanthanum ($_{57}\text{La}$)	30.0
Cobalt ($_{27}\text{Co}$)	30
Neodymium ($_{60}\text{Nd}$)	27.0
Yttrium ($_{39}\text{Y}$)	24.0
Scandium ($_{21}\text{Sc}$)	16.0
Lead ($_{82}\text{Pb}$)	10
Praseodymium ($_{59}\text{Pr}$)	6.7
Thorium ($_{90}\text{Th}$)	6
Samarium ($_{62}\text{Sm}$)	5.3

Elements	Crustal Abundance (parts per million)
Gadolinium ($_{64}\text{Gd}$)	4.0
Dysprosium ($_{66}\text{Dy}$)	3.8
Tin ($_{50}\text{Tn}$)	2.2
Erbium ($_{68}\text{Er}$)	2.1
Ytterbium ($_{70}\text{Yb}$)	2.0
Europium ($_{63}\text{Eu}$)	1.3
Holmium ($_{67}\text{Ho}$)	0.8
Terbium ($_{65}\text{Tb}$)	0.7
Lutetium ($_{71}\text{Lu}$)	0.4
Thulium ($_{69}\text{Tm}$)	0.3
Silver ($_{47}\text{Ag}$)	0.08
Gold ($_{79}\text{Au}$)	0.0031
Promethium ($_{61}\text{Pm}$)	10^{-18}

Lanthanides (lanthanoids), scandium, and yttrium are presented in boldface type.
(Adapted from Wedepohl, 1995)



Why are we interested in them?

- Used in all types of modern electronics and green technologies
- Foreign sources have 95 to 97 percent of the world's current supply
- Make very light and strong permanent magnets, alloys, batteries, catalysts, lighting/displays, lasers, wind turbines, solar panels, etc.
- Limited number of currently developed US sources



Why are we interested in them?

Rare Earth Elements and Their Uses

Element	Applications
Scandium	Metal alloys for the aerospace industry.
Yttrium	Ceramics, metal alloys, lasers, fuel efficiency, microwave communication for satellite industries, color televisions, computer monitors, temperature sensors. Used by DoD in targeting and weapon systems and communication devices. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean energy technologies.
Lanthanum	Batteries, catalysts for petroleum refining, electric car batteries, high-tech digital cameras, video cameras, laptop batteries, X-ray films, lasers. Used by DoD in communication devices. Defined by DOE as near critical in the short-term based on projected supply risks and importance to clean energy technologies.
Cerium	Catalysts, polishing, metal alloys, lens polishes (for glass, television faceplates, mirrors, optical glass, silicon microprocessors, and disk drives). Defined by DOE as near critical in the short-term based on projected supply risks and importance to clean energy technologies.
Praseodymium	Improved magnet corrosion resistance, pigment, searchlights, airport signal lenses, photographic filters. Used by DoD in guidance and control systems and electric motors.
Neodymium	High-power magnets for laptops, lasers, fluid-fracking catalysts. Used by DoD in guidance and control systems, electric motors, and communication devices. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean energy technologies.
Promethium	Beta radiation source, fluid-fracking catalysts.

Element	Applications
Samarium	High-temperature magnets, reactor control rods. Used by DoD in guidance and control systems and electric motors.
Europium	Liquid crystal displays (LCDs), fluorescent lighting, glass additives. Used by DoD in targeting and weapon systems and communication devices. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean energy technologies.
Gadolinium	Magnetic resonance imaging contrast agent, glass additives.
Terbium	Phosphors for lighting and display. Used by DoD in guidance and control systems, targeting and weapon systems, and electric motors. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean energy technologies.
Dysprosium	High-power magnets, lasers. Used by DoD in guidance and control systems and electric motors. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean energy technologies.
Holmium	Highest power magnets known.
Erbium	Lasers, glass colorant.
Thulium	High-power magnets.
Ytterbium	Fiber-optic technology, solar panels, alloys (stainless steel), lasers, radiation source for portable X-ray units.
Lutetium	X-ray phosphors.

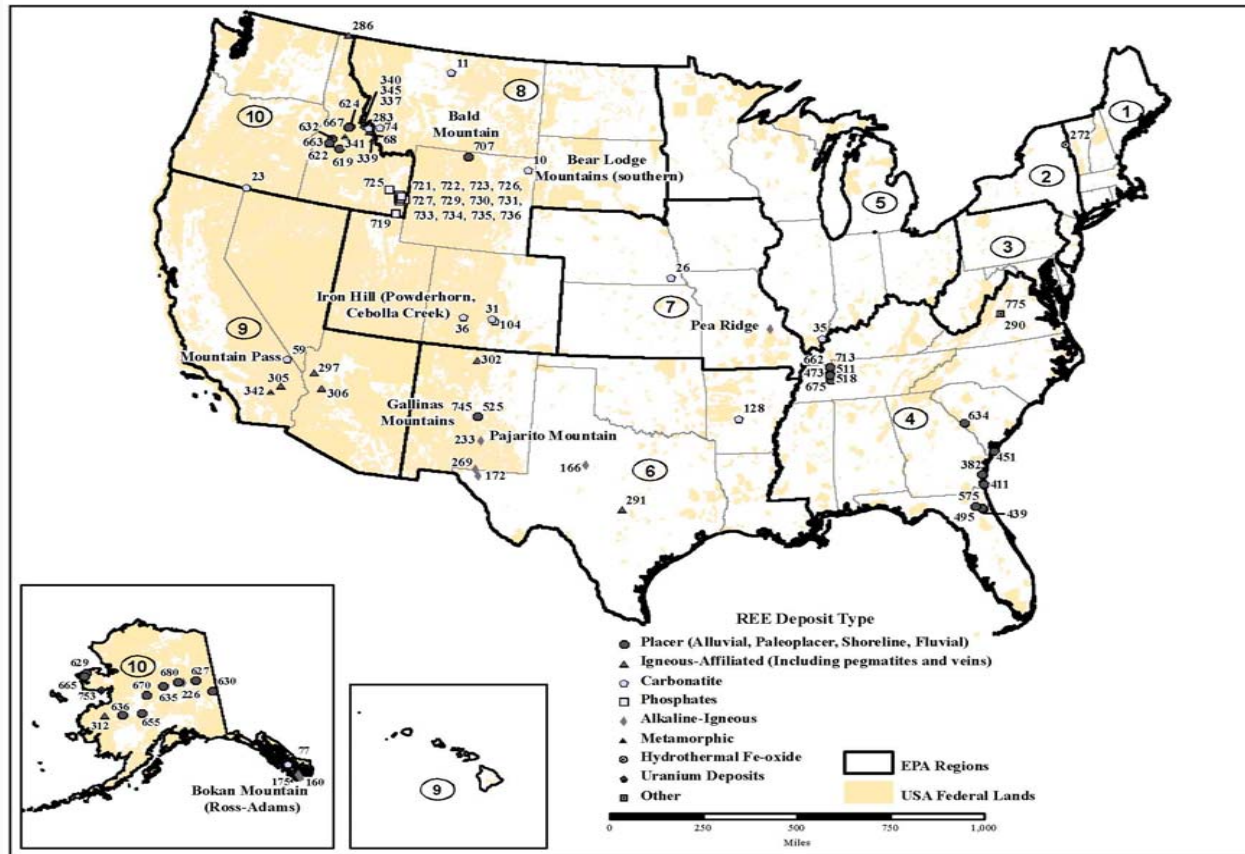
(Adapted from US DOE, 2011)



Where are they found ?

- Everywhere,
-But for economic deposits, see the following map

Where are REE deposits found in the US?



Map showing occurrences of REEs, by rock type (adapted from multiple sources, see Appendix B of EPA ORD NRMRL ETSC REE document)



How are they acquired? Mining?

- Mining – Surface or underground operations with associated surface tailings, impoundments, and processing facilities, etc.
- Resource extraction and processing (hard rock example)
 - Mining = Overburden, Waste Rock, Sub-Ore, and Ore
 - Ore - up to 13 percent REE or greater
 - Tailings - up to 0.5 percent REE or greater
 - Beneficiation = Grinding, flotation, thickening, separation, drying
 - Results in a mineral concentrate – up to 60 percent or greater REO
 - Extraction = Hydrometallurgy, Electrometallurgy, and/or Pyrometallurgy
 - Separates individual REOs from the mineral concentrate
 - Liquid-liquid extraction, solid-liquid extraction, solid phase, ion exchange, supercritical extraction, electrowinning, electrorefining, or electro slag refining
 - Reduction = for high purity rare earth alloys
 - Smelting (metallothermic reduction) is the most widely used method where reductants react in a furnace with oxidants (oxygen, sulfide, carbonate) to separate and free metal
 - Three primary methods to produce REMs = Reduction of anhydrous chlorides or fluorides, reduction of rare earth oxides, fused salt electrolysis of rare earth chlorides or oxide-fluoride mixtures
 - Several other less common processes



How are they acquired? Recycling?

- Collection
 - As of May 2011, 25 state laws require e-waste recycling and 5 states are pending
 - Nationally, 19 percent of consumer electronics were recycled in 2009
 - EPA's Plug-In to eCycling Website includes links to take-back and drop-off locations
 - Partners include retail stores, equipment manufacturers, and mobile device service providers
 - 68 million lbs of consumer electronics were collected and recycled in 2008
- Dismantling/Preprocessing(Separation)
 - Manual or mechanical separation or disassembly, mechanical shredding, and screening
 - Hazardous substances (lead, mercury, other metals, flame retardant resins) and ozone-depleting substances may need to be managed at this stage
- Processing
 - Pyrometallurgy, hydrometallurgy, electrometallurgy, tailings recycling, dry processes using hydrogen gas (research stage), titanium dioxide process (research stage). microbe-filled capsule technology (research stage)
- Commercial REE Recycling applications
 - Number of operations is limited based on a literature review – most are in R&D stage
 - Air conditioners, Washing machines, Hard Disks, Mine Tailings, Batteries, Electronics



What are the Potential Environmental Impacts?

- **Contaminants of concern including metals** - will be dependent on the REE-bearing ore, the toxicity of the contaminants from the waste rock, ore stockpiles, and process waste streams
 - Mobility of the contaminants will be controlled by geologic, hydrologic, and hydrogeologic environments where the mine is located along with the characteristics of the mining process and waste handling methods.
 - Urban mining and/or recycling operations will likely be similar to mineral processing since recovery and refining methods will likely be identical
- **Radionuclides** – are often associated with REE deposits including thorium and uranium
- **REEs** -
 - EPA has conducted an IRIS assessment for cerium (2009) and PPRTVs for gadolinium (2007), lutetium (2007), neodymium (2009), praesodemium (2009), promethium (2007), samarium (2009)
 - Limited information at this time to assess carcinogenic potential
 - EPA has not yet reviewed the toxicity of lanthanum, europium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, scandium, or yttrium
 - Select toxicological and epidemiological data with respect to REEs are published by others in the literature



What are the Potential Environmental Impacts?

Activity	Emission Source (s)	Primary Pollutants of Concern
Mining (aboveground and underground methods)	Overburden Waste Rock Sub-ore Stockpile Ore Stockpile	Radiologicals Metals Mine Influenced Waters/Acid Mine Drainage/Alkaline or neutral mine drainage Dust and Associated Pollutants
Processing	Grinding/Crushing	Dust
	Tailings Tailings Impoundment Liquid Waste from Processing	Radiologicals Metals Turbidity Organics Dust and Associated Pollutants
Recycling	Collection	Transportation Pollutants
	Dismantling and Separation Scrap Waste Landfill	Dust and Associated Pollutants VOCs Metals Organics
	Processing	Dust and Associated Pollutants VOCs Dioxins Metals Organics



What are the Emerging Policies & Alternatives to REEs?

- Emerging Policies/Programs to support REE recycling
 - A Number of Relatively Recently Introduced Congressional Bills, etc. (2010 and 2011)
 - Re-establish domestic REE industry
 - Prohibit export of certain electronics waste
 - Modernize US policies related to production, processing, manufacturing., recycling, and environmental protection – focused on minerals for military security and strong economy
 - Direct DOI to conduct research related to ensuring the supply of critical materials throughout the supply chain
 - DOE ARPA-E - \$30 million in funding to Rare Earth Alternatives in Critical Technologies (REACT)
 - UN – With \$2.5 million in funding from EPA, will track discarded mobile phones and electronic wastes generated in the US to develop solutions aimed at recovering REMs – the project includes other international partners
 - NSF-funded Center for Resource Recovery will develop technologies for greater scrap utilization
- Alternatives to REEs
 - Research
 - Magnets
 - Iron nitride, ferrite, alnico-iron alloy family, iron-cobalt based alloys, and nanostructured compounds
 - Neodymium-iron-boron magnets using less REE and producing less hazardous byproducts
 - Electronic displays - Single-atom-thick sheets of carbon and carbon nanotubes
 - Solar Cells - Copper, zinc, tin, and sulfur



The ORD NRMRL ETSC Document



Project concept discussed on November 18, 2010 at an EPA Technical Support Project meeting

ORD NRMRL ETSC assembled a technical support document development team that participated in monthly calls through September 2011

Internal EPA review leading to a technical support publication by ORD NRMRL ETSC in 2012



Key Findings

Select Key Findings

- Analysis of the future supply and demand for each of the REEs indicates that by 2014, global demand could exceed 200,000 tons per year – which would exceed current production by 75,000 tons per year
- The waste footprint and environmental impacts from mining to extract REE mineral ores are expected to be as significant as current metals/minerals mining practices. The most significant impact from contaminant sources associated with hard rock mining is to surface water and ground water. AMD is not usually a significant issue for REE deposits given their common occurrence with carbonate minerals – however the rock that surrounds or is overlying an ore body may contain sulfide minerals that could create AMD
- Rare earth milling and processing is a complex, ore-specific operation that has potential for environmental contamination when not controlled and managed properly – heavy metals and radionuclides in waste streams
- The specific health effects of elevated concentrations of REEs in the environment from mining and processing REE-containing materials are not well understood - most data reviewed were for mixtures and not individual elements



Suggested Next Steps

Select Suggested Next Steps

- Conduct a more complete literature review of the health, biomonitoring, and ecological impacts literature to build upon the preliminary literature review in this document to ensure all available studies are included
- Support additional human health toxicity and ecological impact studies on specific REEs and use this information to conduct site risk assessments related to REE mining, processing, and recycling
- Expand on this report to develop sustainability studies, systems-thinking, and life cycle assessments for all elements associated with REE mining, processing, and recycling that have the potential for environmental or health impacts to support regional operations
- Convene EPA/federal agencies/industry work shops and information exchanges on topics related to REE technology development, recycling, and impacts



General Notes/Disclaimer

The purpose of this report is to serve as a technical information resource to policy makers and other stakeholders who are concerned with the potential environmental and health effects and impacts that can be identified across the REE supply chain. This document is not a life-cycle assessment or a risk assessment. However, it does, to the extent possible based on anticipated, proposed, or past practices, attempt to identify environmental compartments (i.e., aquatic environment, terrestrial environment, and air) that may be at risk and the corresponding environmental loads (e.g., raw material consumption, air emissions, water discharges, wastes), when that information is available in the literature or an association can be made with anticipated, current, and past practices. The document referenced in this presentation has been subjected to the agency's internal and administrative review and is currently in process for publication as an EPA document. Mention of trade names and/or commercial products in this document and associated presentation does not constitute endorsement or recommendation for use. Any views or opinions expressed by the authors during this presentation on this subject or other subjects may not necessarily represent the views or opinions of the United States of America or the Agency.



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 - James H. Cunningham, Ph.D.
 - Scott A. Guthrie
 - Susan N. Wolf
- Several Other Contributors, Reviewers, and Management Staff



Where to go for more information

Select publications/reports:

- **Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues, U.S. Environmental Protection Agency, Office of Research and Development (To be published in 2012)**
([Web link to be developed](#))
- **Investigating Rare Earth Element Mine Development in EPA Region 8 and Potential Environmental Impacts, U.S. Environmental Protection Agency, Region 8, 2011**
(<http://www.epa.gov/region8/mining/ReportOnRareEarthElements.pdf>)
- **The Principal Rare Earth Elements Deposits of the United States - A Summary of Domestic Deposits and a Global Perspective, U.S. Geological Survey, 2010**
(<http://pubs.usgs.gov/sir/2010/5220/>)
- **Rare Earth Elements - End Use and Recyclability, U.S. Geological Survey, 2011**
(<http://pubs.usgs.gov/sir/2011/5094/pdf/sir2011-5094.pdf>)
- **Critical Materials Strategy, U.S. Department of Energy, December 2011**
(<http://energy.gov/pi/office-policy-and-international-affairs/downloads/2011-critical-materials-strategy>)