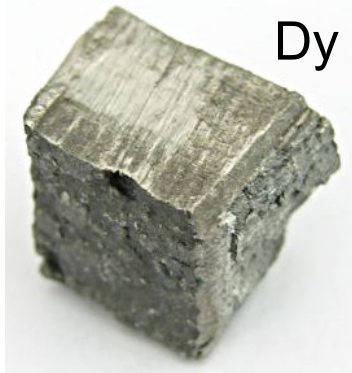


The availability of rare elements for advanced energy technologies

Alex Bradshaw

*Max-Planck-Institut für Plasmaphysik,
Garching/Greifswald und Fritz-Haber-Institut
der Max-Planck-Gesellschaft, Berlin*



Photos: Wikimedia Commons

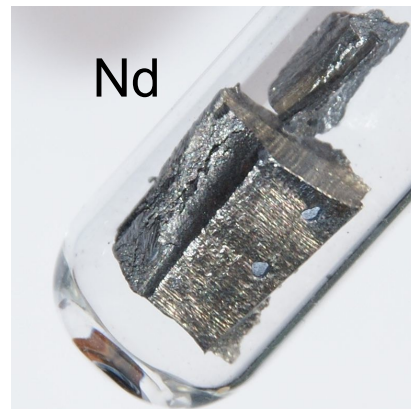


Photo: AMB



Photo: Alpha Ventus



Photo: Wikimedia Commons

Chuquibambilla, Chile: largest open-cast copper mine in the world.
Depth 900 m; length 4.5 km

*Picture removed for
copyright reasons!*

Child labour: mining of columbite-tantalite,
coltan, a so-called conflict mineral,
 $(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta}, \text{Sb})_2\text{O}_6$ in the Congo (DRC)



Photo: REUTERS

Artisanal mining at a
Chinese rare earth
deposit

02.02.2011

Frankfurter Allgemeine
ZEITUNG FÜR DEUTSCHLAND

Vorsorge gegen Rohstoffknappheit

02.02.2011 · EU will Förderung auf eigenem Gebiet verbessern

hmk. BRÜSSEL, 2. Februar. Die EU soll ihre Versorgung mit knappen Industrierohstoffen durch eine gezielte Handelspolitik und die Förderung auf eigenem Gebiet verbessern. Die Europäische Kommission hat die Mitgliedstaaten am Mittwoch in Brüssel bei der Vorstellung ihrer neuen Rohstoffstrategie aufgefordert, die Hürden für die Genehmigung des Abbaus

07.12.2011

Bloomberg Our Company | Professional | Anywhere

HOME QUICK NEWS OPINION MARKET DATA PERSONAL FINANCE TECH POLITICS S

Lithium, Cobalt Among Minerals Facing Chronic Shortage, PwC Says

By Jesse Riseborough - Dec 7, 2011 1:00 AM GMT+0100

f t in +1 0 COMMENTS

QUEUE

Global manufacturers may face a critical shortage of 14 raw materials over the next five years affecting industries including chemicals, aviation and renewable energy, according to PricewaterhouseCoopers LLP.

Handelsblatt

21.06.2012

Rohstoff-Knappheit bedroht Deutschlands Industrie

Deutschlands Industrie ist auf die Versorgung mit Rohstoffen angewiesen. Doch die Ressourcen sind knapp, die Preise von wichtigen Grundgütern steigen. Die Abhängigkeit von Importen bedroht die heimische Wirtschaft.

Düsseldorf. Für Deutschlands Unternehmen wäre es ein Horrorszenario: Die Versorgung mit Rohstoffen ist abgebrochen, die Energiequellen versiegt. Binnen kürzester Zeit stünden die Bänder in den Fabriken still, die Produktion würde zum Erliegen kommen. Am Ende geht beim Exportweltmeister Deutschland das Licht aus.



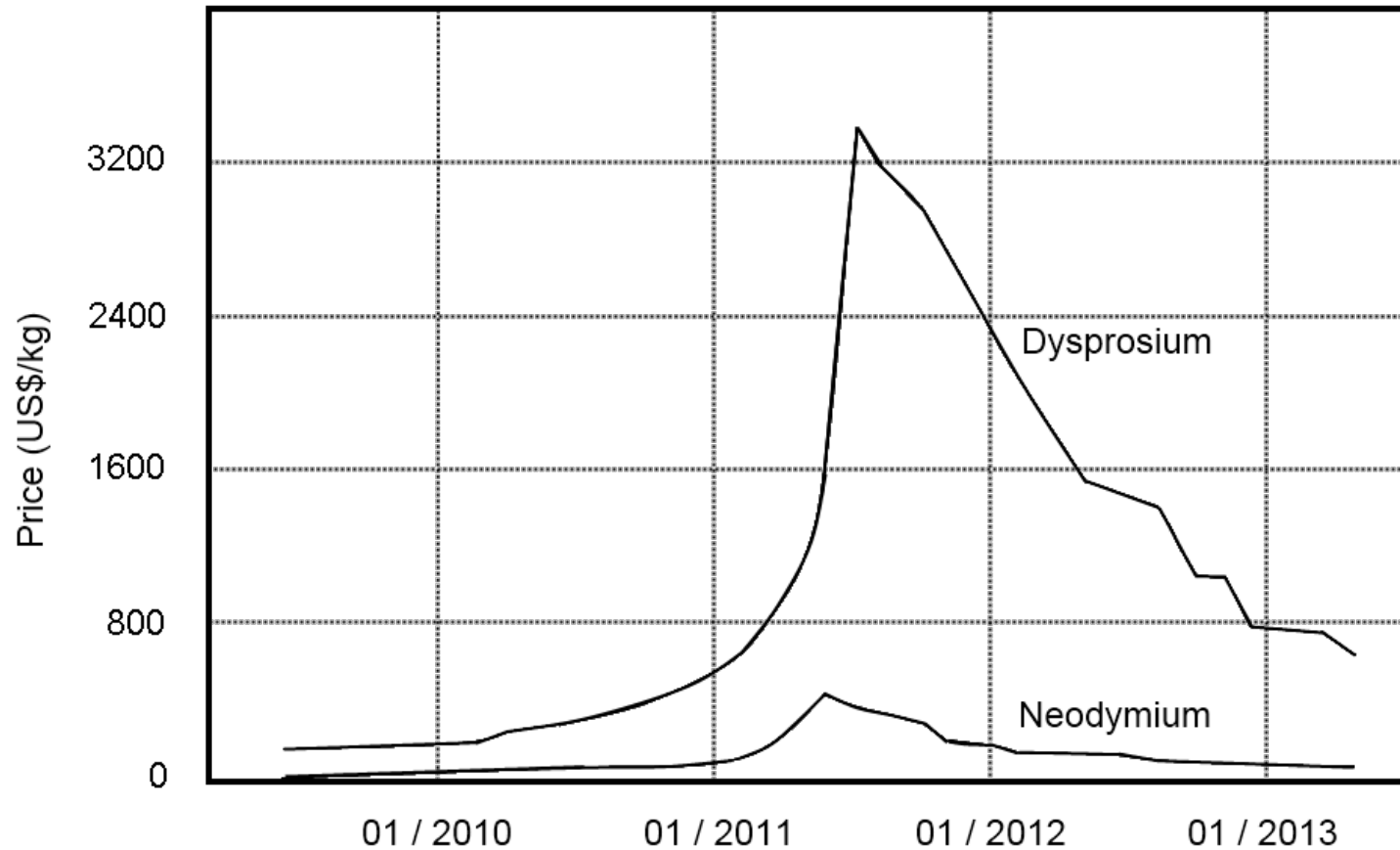
What is scarcity?

Can only be defined in economic terms: Supply cannot satisfy demand, which leads to higher prices. There can be various reasons:

- sudden, sharp increases in demand due, for example, due to fast economic growth, new technologies
- obstacles to investment on the supply side
- environmental problems, natural disasters
- the element concerned is a by-product
- geopolitical problems
- **geochemical scarcity**
Is it possible that mineral depletion is already playing a role?



REE: speculative „bubble“ 2011/2012



Price development for the REE dysprosium and neodymium in the period 2009-2013 (FOB China). Bradshaw et al, DPG Proceedings Dresden (2013) based on data from the Magnet Energy Corporation



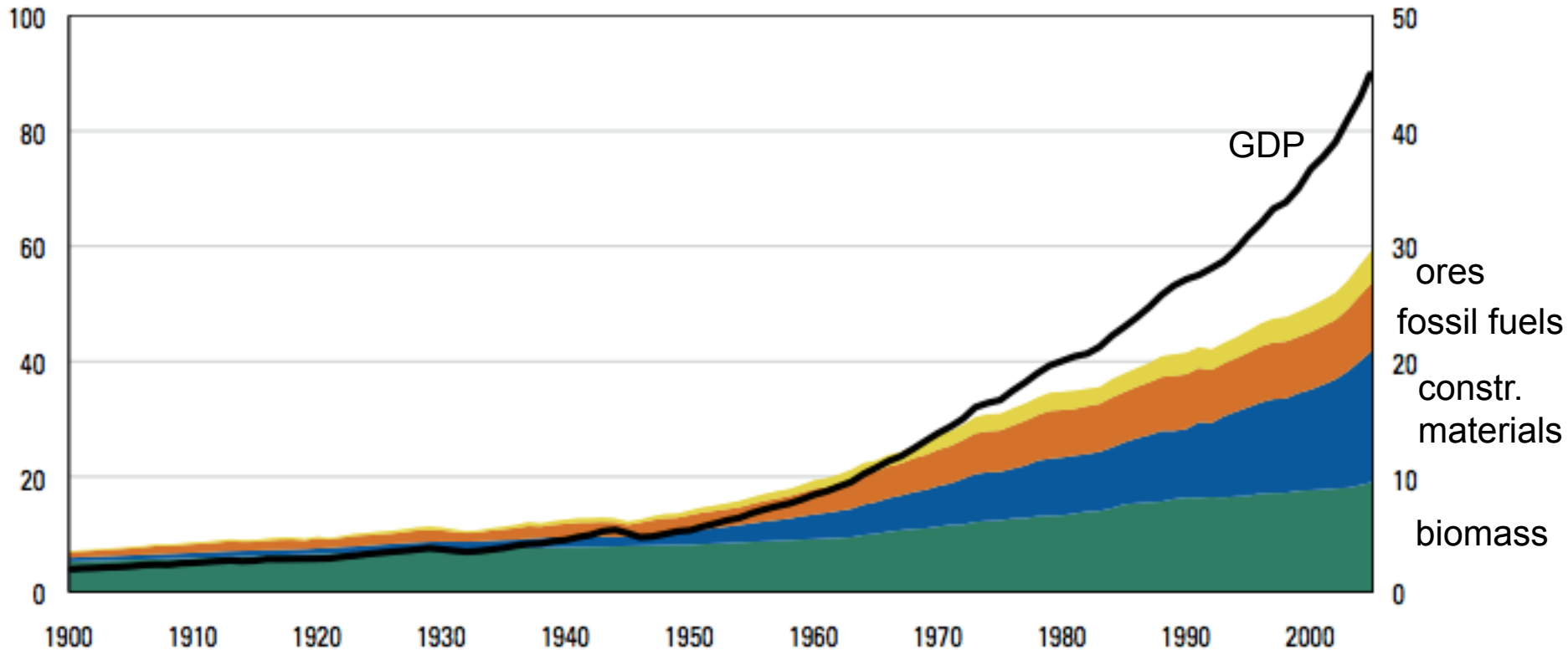
How fast are we using natural resources?



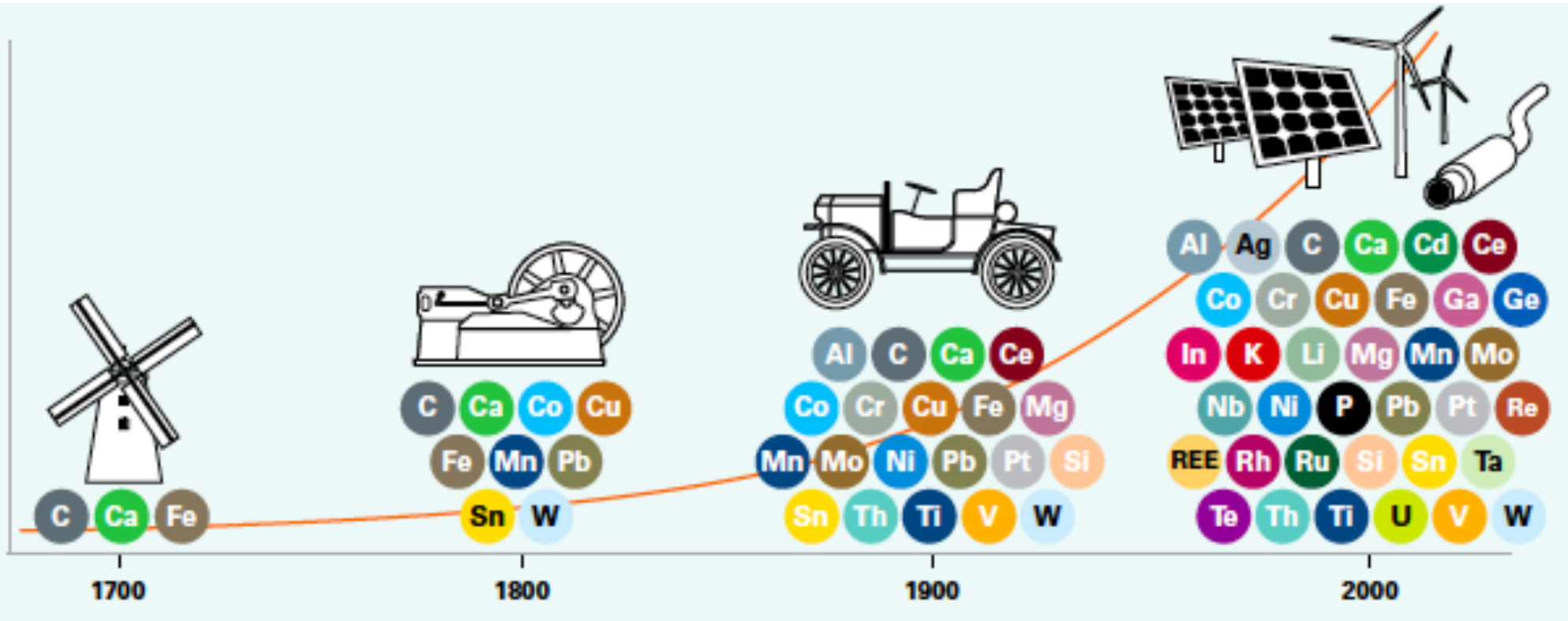
1900-2010 Increase of factor 8 in consumption of global resources;
biomass 4, fossil fuels 12, **ores 27**, construction materials 34.

Material extraction
 10^9 tons

GDP 10^{12} \$



After Krausmann et al 2009, UNEP report on "Decoupling"



Graphik: Reller, Achzet et al, *Materials critical to the energy industry*, 2nd Ed, Universität Augsburg (2014)



Bild: FORUM: Das Wochenmagazin

It is estimated that a mobile phone contains about 50 different elements, including Ag, Au, Pd, Cu, Ni, Pb, Bi, As, Sb, Sn, Te, In, Be, Ca, Al, Cd, Si, Ti, Mn, Fe, Co, Zn, Mo, Ge, Ru, Ba, Ta, W und Zr.

Total global mobile phone sales to date ca. 12 billion (2012):
2500 t Ag, 240 t Au und 90 t Pd!



What does „rare“ mean?

Geochemically abundant elements: Al, Fe, Mg, Mn, Si, Ti
Concentration in the Earth's crust exceeds 0.1% by weight
(1000 ppm)

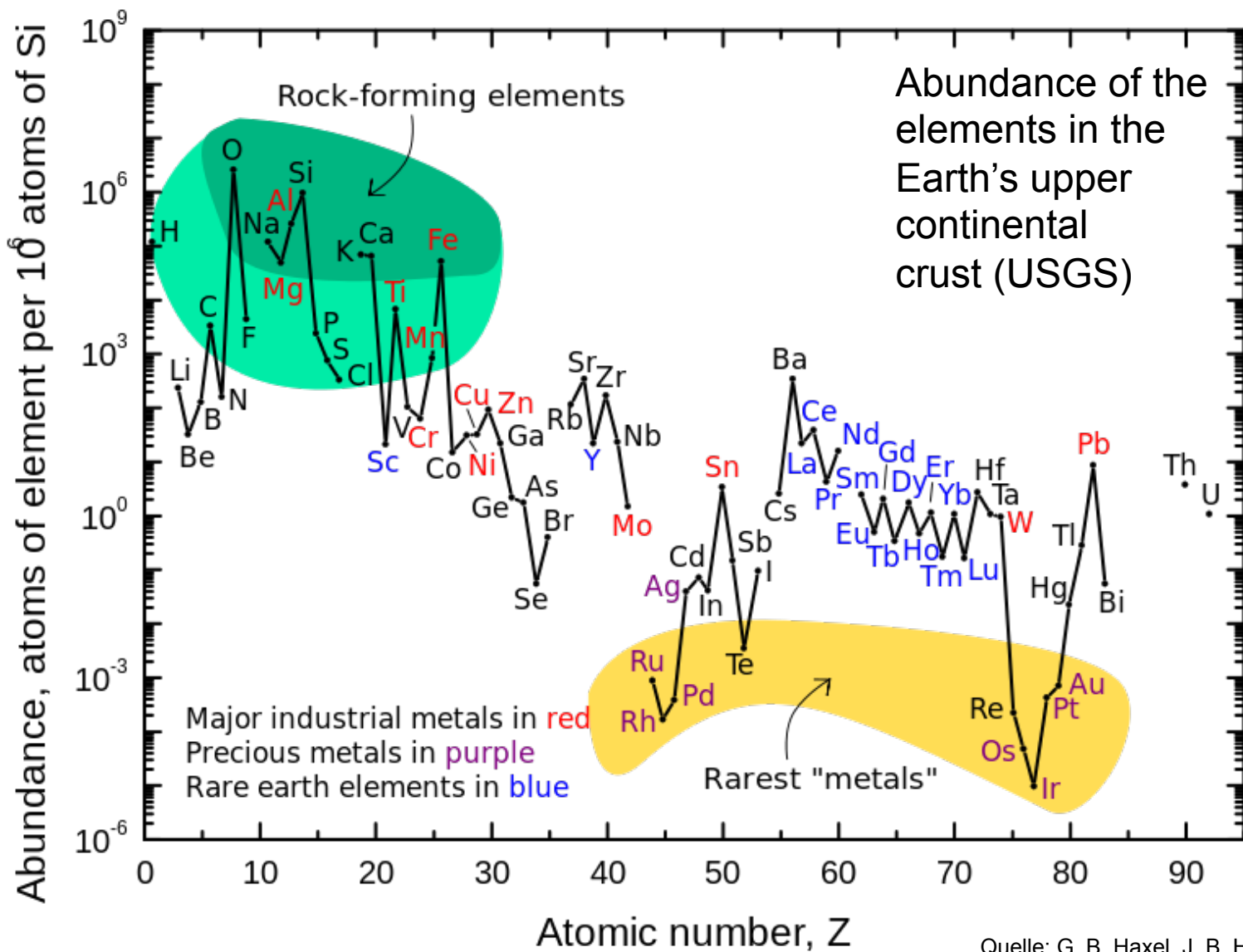
Geochemically “rare” elements (under 1000 ppm):

- ferro-alloy metals, e.g. Co, Ni, W
- base metals, e.g. Cu, Pb, Hg
- precious metals, e.g. Au, Ag, Pt
- speciality metals, e.g. Li, In, Ta, rare earths

Is “rare” the correct word? Iridium is probably the element with the lowest concentration in the crust, ≈ 0.01 ppb (10^{-11}).

Mass of the continental crust: 10^{19} tons.

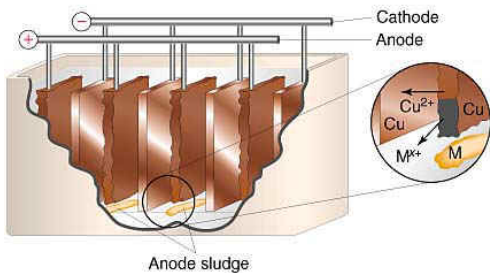
Thus, 10^8 tons of iridium are in principle available



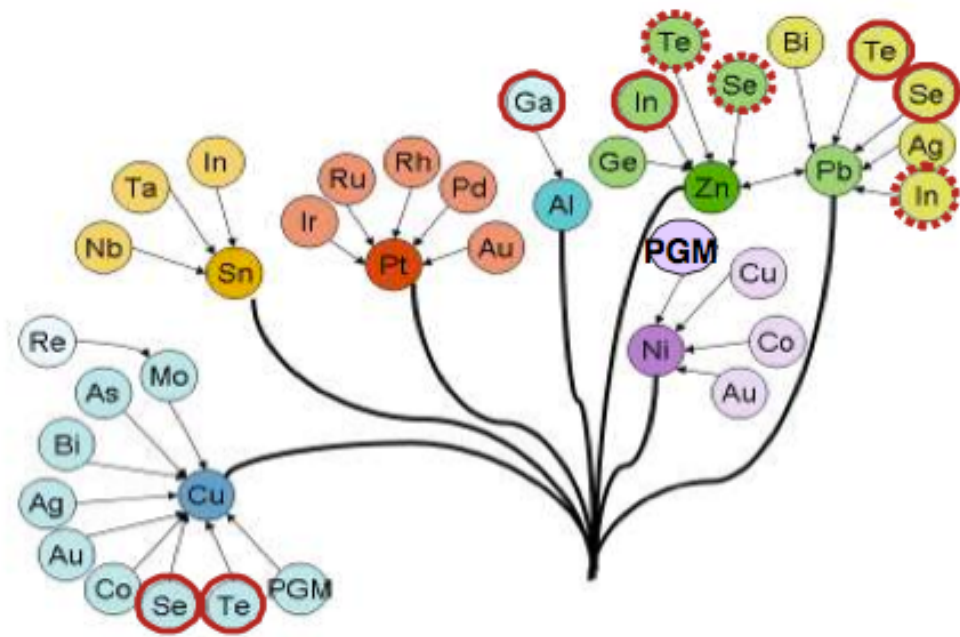
Quelle: G. B. Haxel, J. B. Hedrick and G. J. Orris, US Geological Survey, 2005

Typical “by-product” metals are found in the ores of “carrier” metals at the ppm level.

e.g. Tellurium produced mainly from anode slimes in the electrolytic refining of copper.
1 t Cu produces 1 g Te.



Source: corrosion-doctors.org



Source: Hagelüken und Meskers, umicore

D. Meadows et al, 1972. *The Limits to Growth: A report for the Club of Rome’s project on the predicament of mankind*

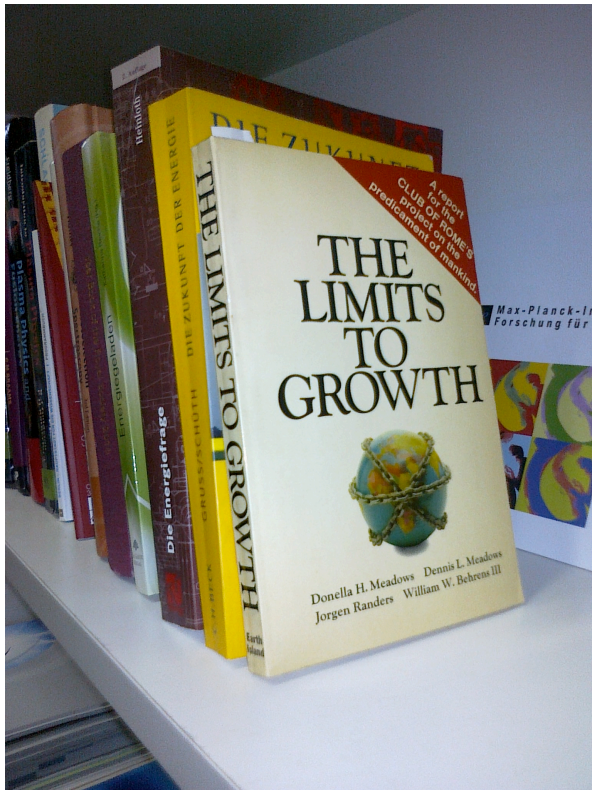


Photo: AMB

Meadows and co-workers took 19 raw materials, including coal, oil and natural gas and calculated the “static lifetime” (reserves divided by annual consumption) and the “dynamic lifetime” (same, but assuming exponential growth).

Their conclusion: *“Given present resource consumption rates and the projected increase in these rates, the great majority of the currently important non-renewable resources will be extremely costly in 100 years from now.”*



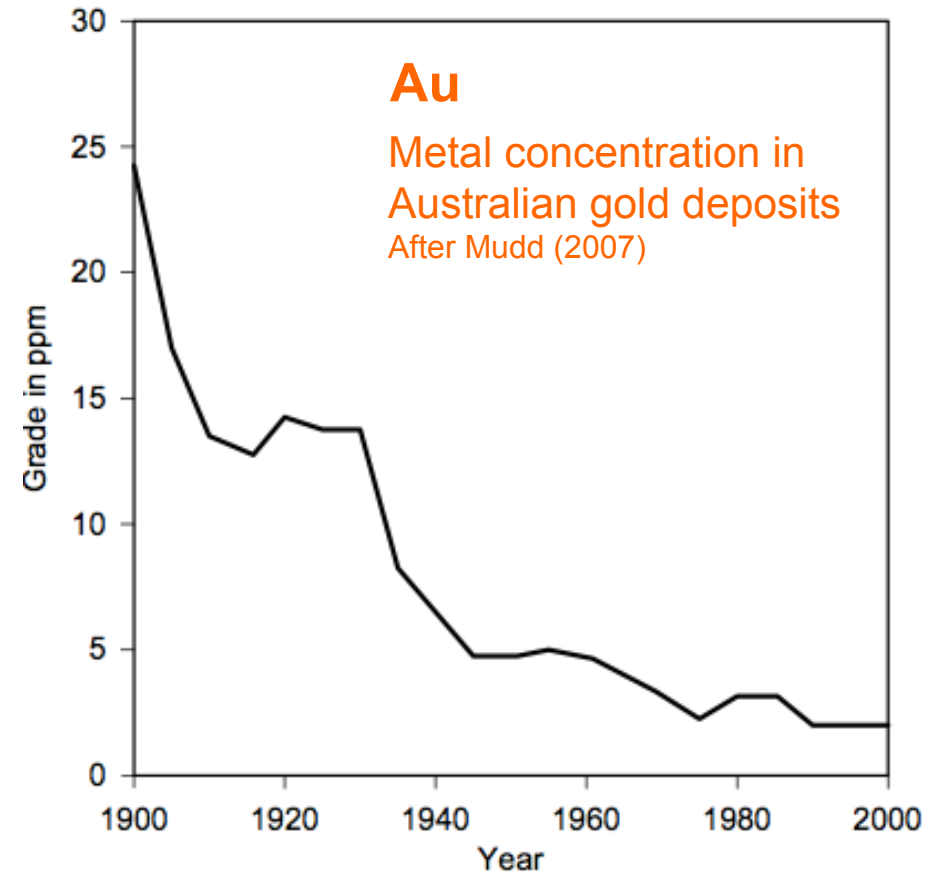
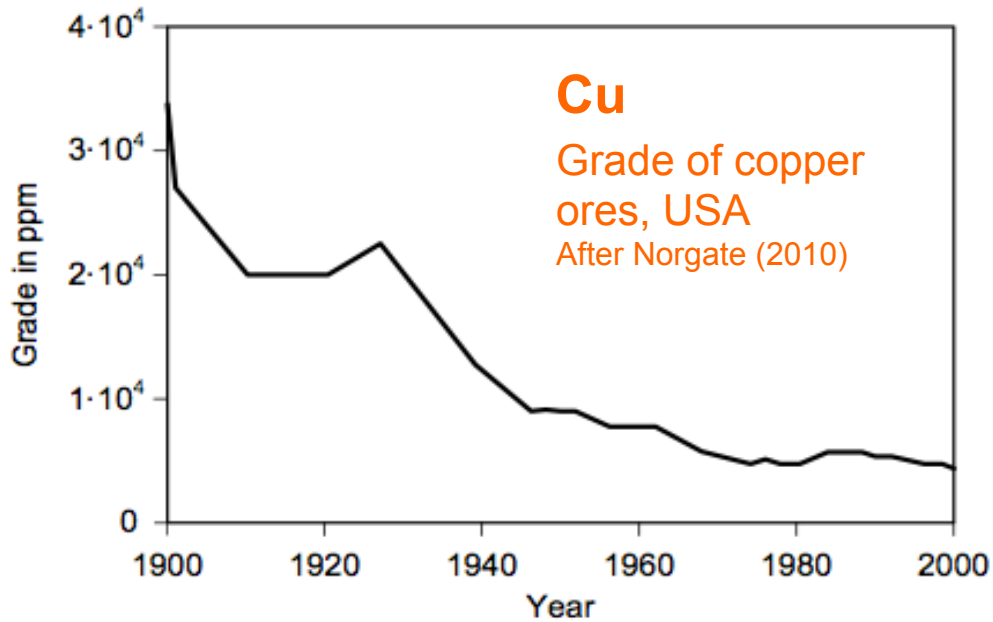
The optimists (also known as the “cornucopians”) say “NO”:

1. The potential resources in the Earth's crust are enormous, even for the rarest elements, e.g. tellurium 0.001 ppm ($= 10^{-9}$) $\approx 10^{10}$ tons!
2. Metals and other elements in the Earth's crust are indestructible; they will not be used up. Recycling is possible.
3. There is also substitution, i.e. using another, less rare element with perhaps less than optimal properties. Taken *ad extremum*: unlimited, or infinite, substitutability (Solow, Goeller and Weinberg).

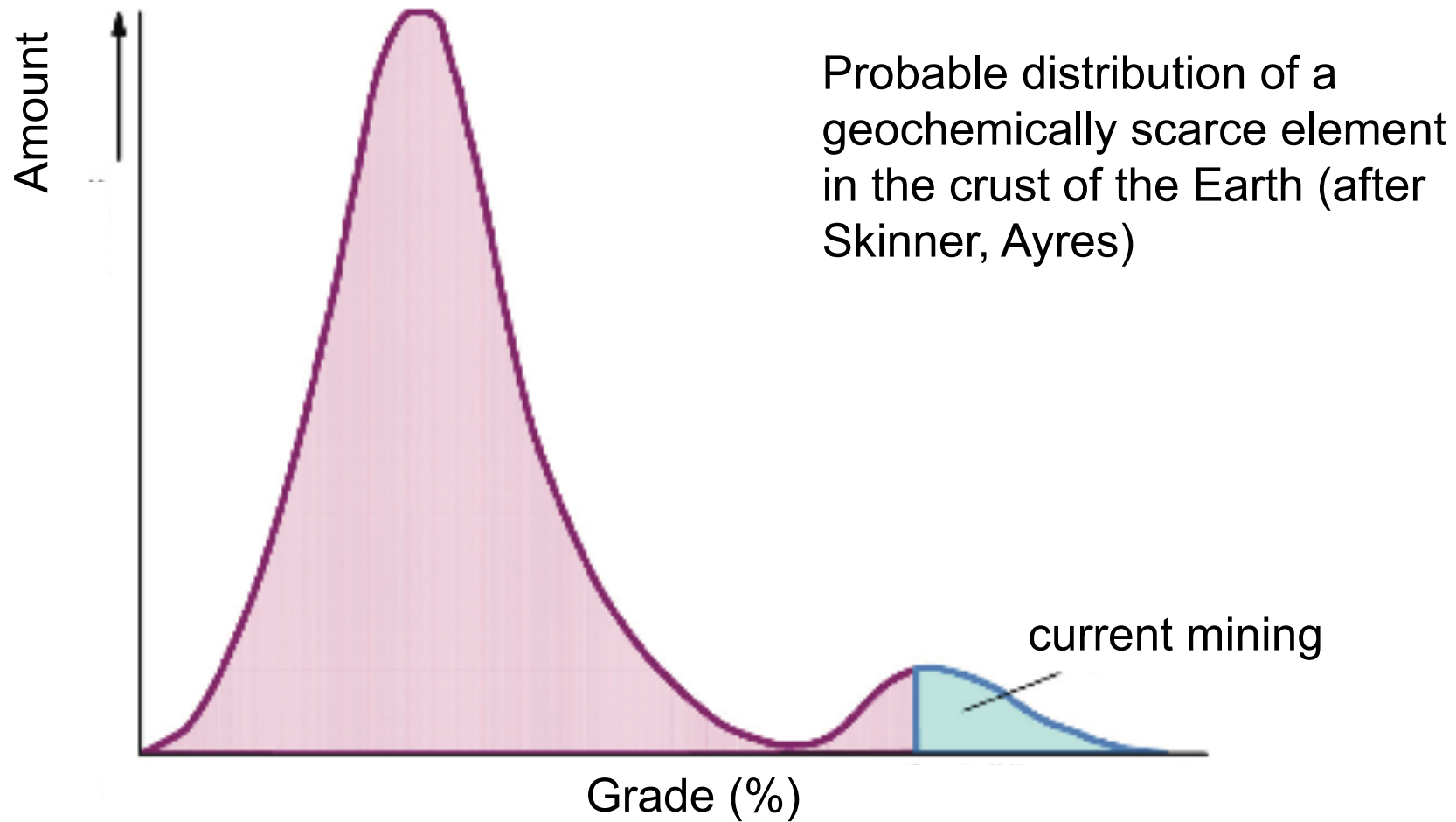
The pessimists say YES:

1. Mineral resources are indeed finite. The first signs of mineral scarcity are already apparent. Examples gold and copper. Skinner thesis.
2. As ore of lower grade is mined, more energy and water are required, and environmental damage increases.
3. Recycling never 100%.
4. Vast increase in the amount of in-use stock *“An American world of 10 billion people”* (Ernst, 2002) by the end of the century.
5. The postulate of unlimited substitutability is deeply flawed: the different elements have unique properties, many of which may be important for future generations.

Decreasing grade



In a particular region the average grade of ore mined decreases as a function of time, since the “best” deposits will be exhausted first.



The pessimists say YES:

1. Mineral resources are indeed finite. The first signs of mineral scarcity are already apparent. Examples gold and copper. Skinner thesis.
2. As ore of lower grade is mined, more energy and water are required, and environmental damage increases.
3. Recycling never 100%.
4. Vast increase in the amount of in-use stock *“An American world of 10 billion people”* (Ernst, 2002) by the end of the century.
5. The postulate of unlimited substitutability is deeply flawed: the different elements have unique properties, many of which may be important for future generations.

The truth lies somewhere in the middle:

- Total depletion will never occur. There will always be minerals in the Earth's crust or in the oceans.
- However, sooner or later a point will be reached when – due to partial depletion – the energy required (or the quantities of water) will be so large and the environmental problems so severe, that we will have to stop.
- Is it fair to leave such a situation as a legacy to future generations?

The next few decades will be characterised by a massive shift away from fossil fuels towards renewable energy forms and, perhaps in some countries, towards nuclear.

There will still be a high demand for raw materials, mainly for the production, transmission, storage and utilisation of energy obtained from regenerative sources.

Examples of “energy materials”:

- Rare earth elements for synchronous motors in wind turbines and electric cars
- Cd, Te, In, Ga, Se for solar cells
- Li, Co for batteries
- Li, Be, He for nuclear fusion
- PMG for fuel cells



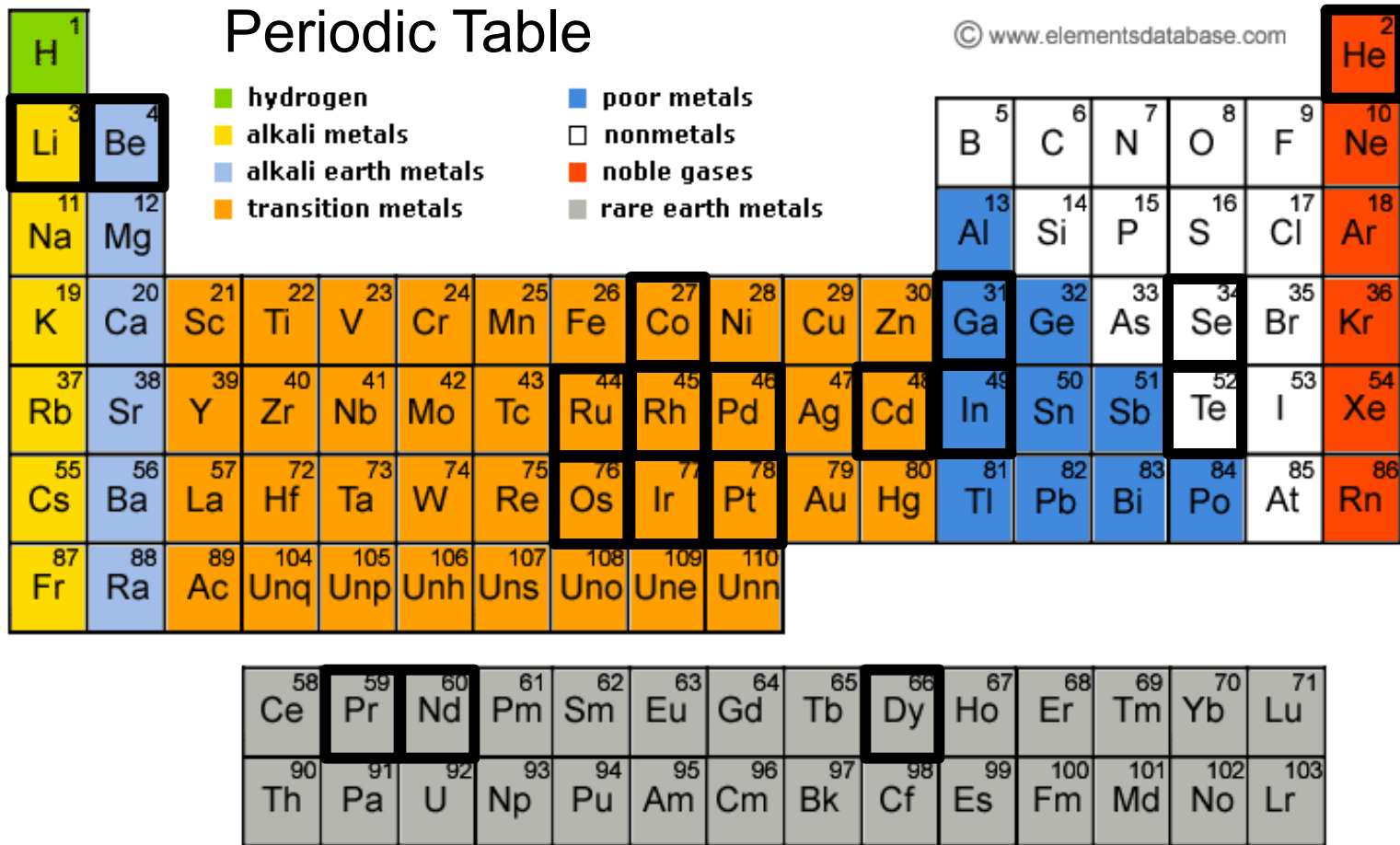
Photo: Wikimedia Commons



Photo: Solar Power Plant Information Center



so-called energy-critical elements



Reserves und resources

“Reserves” are the deposits of the element in the continental crust which can be extracted economically at the present time.

Picture removed for copyright reasons!

“Resources” are the deposits of the element in the continental crust, for which extraction is technically possible, but not (yet) economically feasible.

The resources can be divided into “identified” and “undiscovered”, whereby the latter category can be further sub-divided into “hypothetical” and “speculative”.

Figures are published every year, amongst others, by the US Geological Survey (USGS).

CdTe Thin film photovoltaic cells (6.2 % market share 2012)

Cadmium: Rare. Continental crust: 0.2 ppm. Ni-Cd batteries, but no longer in the EU! By-product in the mining of Zn (0.3% in sphalerite, ZnS). Annual production 28 kt. Reserves 640 kt, resources \approx 5 Mt. Static lifetime 23 y.

Tellurium: Very rare. Crust: 0.0001 ppm. By-product in the extraction of Cu und Pb. Annual production \approx 500 t. Reserves 24 kt, resources \approx 100 kt(?).

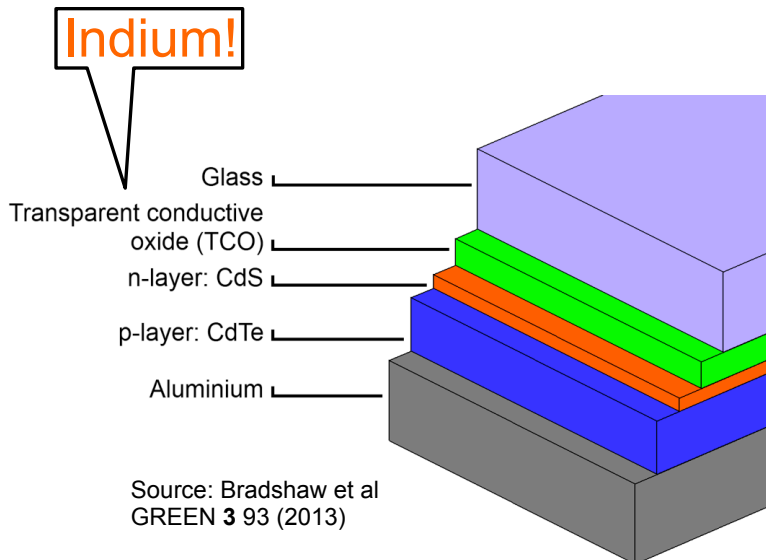


Foto: Solar Power Plant Information Center

Waldpolenz Solar Park, Sachsen
CdTe (First Solar)



CI(G)S thin film photovoltaic cells (3.4% market share 2012)



Module efficiency 12-14 %, compared to 10-12 % and 6-9 % for CdTe and a-Si, respectively.

Indium: Very rare. Crustal abundance 0.1 ppm. By-product of Zn (0.01% in sphalerite, ZnS). Annual production \approx 1.8 kt. Main use (>50%) for LCD, touch panels, LED's etc. Reserves: 11 kt, resources unknown. Static lifetime 6 years.

Gallium: Rare. Crustal abundance 15 ppm. By-product in the extraction of Al from bauxite. Annual production \approx 300 t. Reserves unknown (proprietary!), resources \approx 1 Mt. Static lifetime unknown,

Selenium: Very rare. Crustal abundance 0.05 ppm. Like Te, by-product in the electrorefining of Cu. Annual production 3.5 kt. Reserves \approx 92 kt. Resources unknown. Static lifetime 26 years.



Neodymium, praseodymium, dysprosium

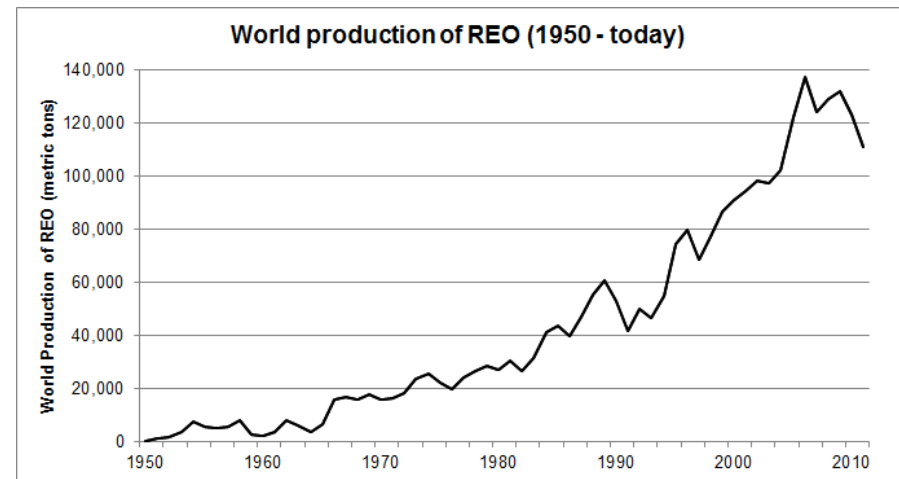
REE occur mainly in the minerals monazite, CeYPO_4 , and bastnaesite, CeFCO_3 . Are they really “rare”? Range from Ce (83 ppm) to Lu (0.8 ppm). Only a few rich deposits. Reserves: 110 Mt (Dy only 1% thereof). Resources considerably more extensive. Annual production: 110 kt, static lifetime 1000 years.

$\text{Nd}_2\text{Fe}_{14}\text{B}$ is used as permanent magnet material in synchronous electric machines in wind turbines (2011: 14% market share) and in the automobile industry. Quantitatively, ca. 100 - 200 kg REE pro MW.



The rare earth mine in Bayan Obo, Inner Mongolia autonomous region.

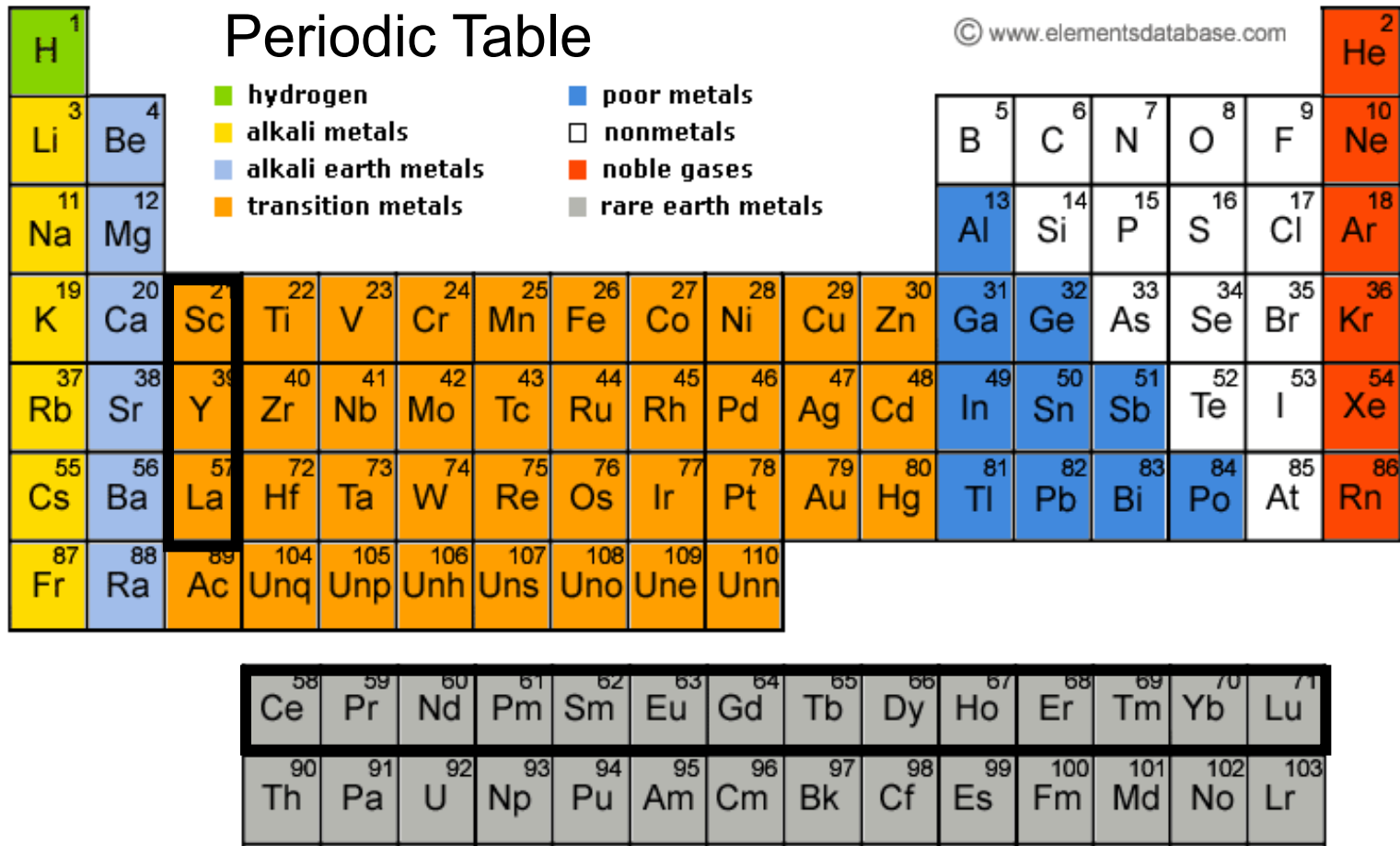
Foto: Wu Changqing (China Daily)



Source: Bradshaw et al, *GREEN* (2013) based on USGS data

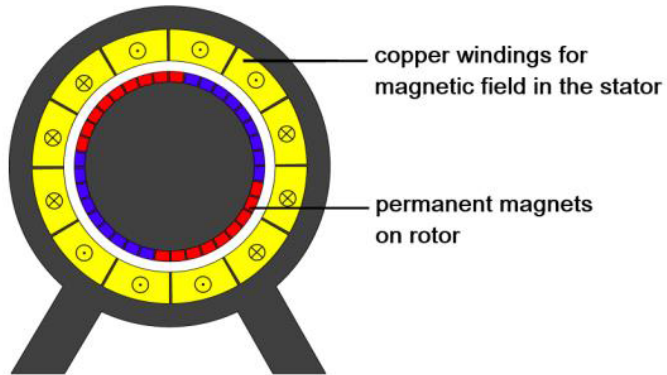


The 17 rare earth elements

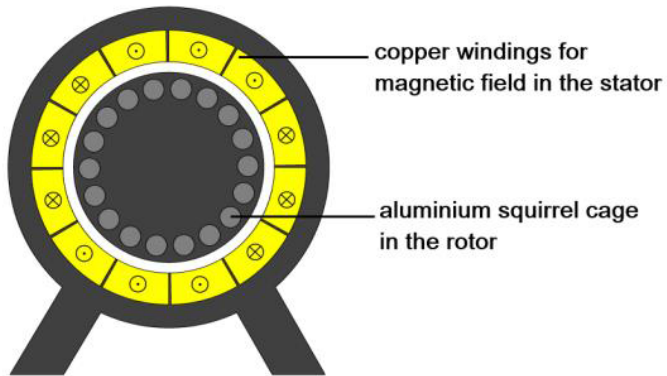




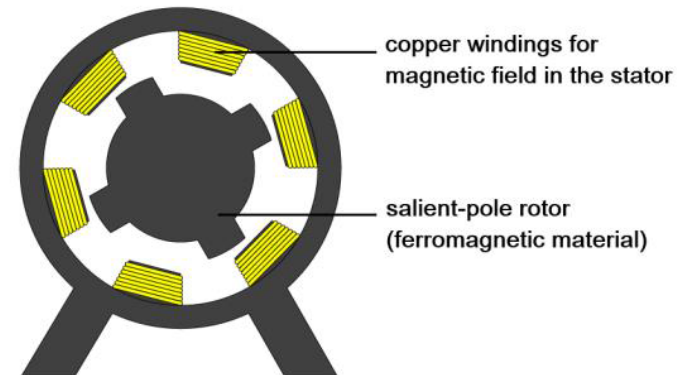
Three types of electric motor



a) Permanent magnet synchronous motor



b) Asynchronous, or induction motor

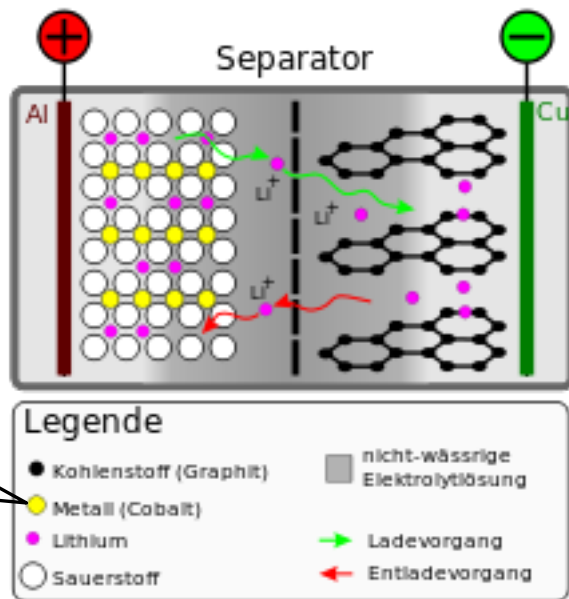


c) Switched reluctance motor

After Bradshaw et al,
GREEN 3 93 (2013)

Lithium

Not rare. Crustal abundance 20 ppm. Two major sources of lithium: minerals, z.B. spodumene, $\text{LiAlSi}_2\text{O}_4$, and the *salare* in the Andes and Himalayas. Uses: glass and ceramics 29%, **batteries 27%**. Annual production: 34 kt. Reserves 13 Mt, resources 30 Mt. Static lifetime 380 yrs. 10 Mt to electrify global automobile fleet?



cobalt!

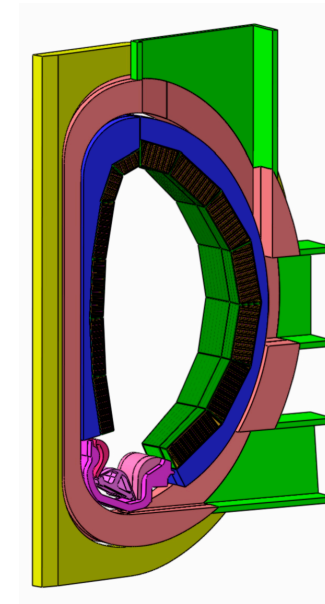
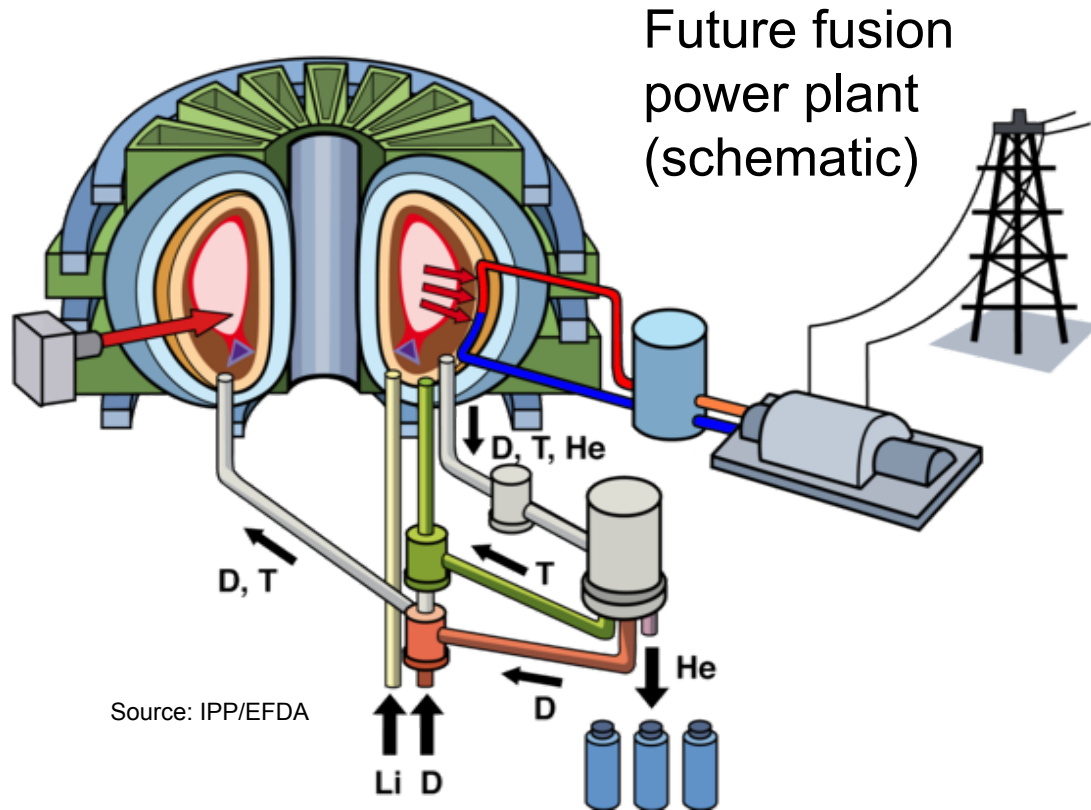
Schematic of a lithium ion battery (positive electrode: LiCoO_2 ; negative electrode: Li graphite).
(source: <http://www.stromtip.de>)

Salar de Uyuni, Bolivia: 5 Mio. t Lithium



Foto: SGW@raphme

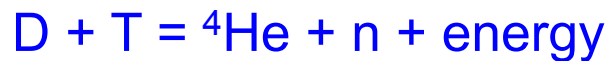
Note that **Lithium** will also be needed for nuclear fusion!



Source: Bradshaw et al, Fusion Eng. Des. **86** 2770 (2011)

DEMO torus sector (11.25°) with integrated HCLL blanket modules

Fusion reaction:



Tritium breeding reaction:



But a neutron multiplier is also needed
(Be or Pb), e.g. ${}^9\text{Be} + n = {}^2\text{He} + 2n$



Beryllium

Rare (ca. 2 ppm in the Earth's crust), but hardly any deposits.
Annual production: 240 t (2011). No reliable figures for reserves.
Resources: 80.000 t (?).

Helium

Obtained from the fractional distillation of natural gas (concentration between 0.01 und 1 %). Required for cryogenics (e.g. magnets for magnetic resonance tomography), as a protective gas, for nuclear fusion* (magnets and coolant) and in some planned G4 fission reactors.

*Note that in theory fusion reactors will actually produce helium! But the losses from an inventory of ca. 50 tons are expected to be much greater.

Order of magnitude calculation: Ca. 5000 fusion power plants (1 GWe) for 30 % of global electricity supply: ${}^6\text{Li}$ burn-up 1.5 kt p.a., Be burn-up 0.5 kt p.a.



Assumption 1: 60 % contribution of renewables to global energy production (corresponds to one of the aims of the German “Energiewende”, but here globally) → ca. 150 000 TWh

Assumption 2: Contributions of 30 % wind, 30 % PV (one third each CdTe and CIGS), 30 % solar thermal, 10 % others.

Wind

Installed power would have to be ca. 10 TWp with a capacity factor of 50 %. 100 – 200 kg/MWp Nd, Pr und Dy would be needed for synchronous generation with permanent magnets → **1 – 2 Mt** „in-use stock“ 2050

Photovoltaics

Installed power would have to be 6 TWp each für CdTe und CIGS with 25% capacity factor. Gives „in-use stock“ 2050 →

Cd, Te ca. 0.5 Mt **In ca. 0.1 Mt**, **Ga ca. 0.04 Mt**, **Se ca. 0.3 Mt**

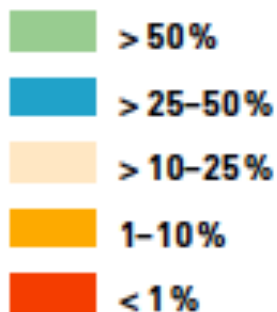


Can we use raw materials more efficiently?

- Higher efficiency of mining, beneficiation and utilisation
- Making use of previous waste
- Re-use and recycling, including recycling-oriented design.
How successful is recycling at present? UNEP report!
- Substitution
- Changes of attitude



End of Life Recycling Rate (EoL-RR) for 60 metals



1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	**	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra		Rf	Db	Sg	Sg	Hs	Mt	Ds	Rg	Uub	Uut	Uug	Uup	Uuh	Uus	Uuo

Source: T. Graedel, C. Hagelüken et al, *Recycling Rates of Metals*, UNEP Report (2011)

* Lanthanides	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
** Actinides	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Bild: FORUM: Das Wochenmagazin

It is estimated that a mobile phone contains about 50 different elements, including **Ag** (ca. 1500 ppm), **Au** (ca. 300 ppm), **Pd** (ca. 100 ppm), **Cu** (ca. 10%), **Ni** (ca. 2%), **Pb** (ca. 0.2%), **Bi**, **As**, **Sb**, **Sn**, **Te**, **In**, **Be**, **Ca**, **Al**, **Cd**, **Si**, **Ti**, **Mn**, **Fe**, **Co**, **Zn**, **Mo**, **Ge**, **Ru**, **Ba**, **Ta**, **W** und **Zr**. (“Easily” re-cyclable in **red!**)

Total global mobile phone sales to date ca. 12 billion (2012):
2500 t Ag, 240 t Au und 90 t Pd!

Not like this ...



Recycling electronic waste in New Dehli
Quelle: Wikimedia Commons



Workers in a recycling yard in China
Quelle: Euronews

But rather...



Source: UMICORE

**UMICORE: new battery recycling
plant, Hoboken, Belgium**



- Seen from our present perspective, most of the rare elements that that might be crucial for the energy transformation (“Energiewende”) are in principle readily available.
- Mineral depletion causing “geochemical scarcity” is unlikely to take place in the foreseeable future, although mining will become more difficult, costlier and cause considerably more damage to the environment.
- Note, however, that some metals, e.g. Te and In, may become scarce, since they are by-products in the extraction of metals mined in larger quantities (in this case, Cu and Zn, respectively).
- We can stave off mineral depletion – although not indefinitely – by measures such as higher efficiency, re-use/recycling and substitution. But remember the welfare of future generations!



Photo: SGW@raphme

Salar de Uyuni, Bolivia: 5 Mt lithium

