The availability of rare elements for advanced energy technologies

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Photos: Wikimedia Commons

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Photo: AMB

Photo: Alpha Ventus
Chuquicamata, Chile: largest open-cast copper mine in the world. Depth 900 m; length 4.5 km
Child labour: mining of columbite-tantalite, coltan, a so-called conflict mineral, \((\text{Fe,Mn})(\text{Nb,Ta,Sb})_2\text{O}_6\) in the Congo (DRC)
Apparently there is a serious shortage of raw materials!

**Frankfurter Allgemeine**

**02.02.2011**

Vorsorge gegen Rohstoffknappheit

02.02.2011 · EU will Förderung auf eigenem Gebiet verbessern

**Bloomberg**

Lithium, Cobalt Among Minerals Facing Chronic Shortage, PwC Says

07.12.2011

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.

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

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”
Elements for the production, distribution and storage of energy

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
Abundance of the elements in the Earth’s upper continental crust (USGS)

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.
Meadows and “The Limits to Growth” 1972

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

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

Should we be worried about depletion of the Earth’s mineral resources?
Should we be worried about depletion of the Earth’s mineral resources?

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.
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 Skinner thesis

Probable distribution of a geochemically scarce element in the crust of the Earth (after Skinner, Ayres)
Should we be worried about depletion of the Earth’s mineral resources?

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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?
Materials for the energy transformation

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
so-called energy-critical elements

Periodic Table

<table>
<thead>
<tr>
<th>Periodic Table</th>
<th>hydrogen</th>
<th>alkali metals</th>
<th>alkali earth metals</th>
<th>transition metals</th>
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<th>nonmetals</th>
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<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
</tr>
</tbody>
</table>

Varenna July 2014
Reserves und resources

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

“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).
Energy materials: CdTe

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 ≈ 5 Mt. Static lifetime 23 y.

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

Source: Bradshaw et al GREEN 3 93 (2013)
Energy materials: CI(G)S

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

{Cu(In$_x$Ga$_{1-x}$)Se$_2$} and CuInSe$_2$

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$_4$, und 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.

Nd$_2$Fe$_{14}$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 17 rare earth elements

Periodic Table

- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- rare earth metals
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)
Energy materials: lithium

**Lithium**

Not rare. Crustal abundance 20 ppm. Two major sources of lithium: minerals, z.B. spodumene, LiAlSi$_2$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?

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!
Lithium and beryllium in future nuclear fusion reactors

Future fusion power plant (schematic)

Source: IPP/EFDA

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

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

Fusion reaction:
\[ D + T = ^4\text{He} + n + \text{energy} \]

Tritium breeding reaction:
\[ ^6\text{Li} + n = ^4\text{He} + T \]

But a neutron multiplier is also needed (Be or Pb), e.g.
\[ ^9\text{Be} + n = 2^4\text{He} + 2n \]
**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: $^6$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


<table>
<thead>
<tr>
<th>Element</th>
<th>Recycling Rate</th>
</tr>
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<tbody>
<tr>
<td>Li</td>
<td>&gt;50%</td>
</tr>
<tr>
<td>Na</td>
<td>&gt;25-50%</td>
</tr>
<tr>
<td>K</td>
<td>&gt;10-25%</td>
</tr>
<tr>
<td>Rb</td>
<td>1-10%</td>
</tr>
<tr>
<td>Cs</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Ba</td>
<td>**</td>
</tr>
</tbody>
</table>

**Lanthanides:**
- La
- Ce
- Pr
- Nd
- Pm

**Actinides:**
- Ac
- Th
- Pa
- U
- Np
- Pu
- Am
- Cm
- Bk
- Cf
- Es
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!
Recycling

Not like this ...

Recycling electronic waste in New Delhi
Quelle: Wikimedia Commons

But rather...

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

Workers in a recycling yard in China
Quelle: Euronews
Some conclusions

• Seen from our present perspective, most of the rare elements 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!
Salar de Uyuni, Bolivia: 5 Mt lithium

Photo: SGW@raphme