LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complex & POM, MOF, MLD
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Pt metals & Magnetism
12.	Wed	13.10.	Co, Ni, Cu & Superconductivity
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021 (in ZOOM) at 9.00 – 12.00

PRESENTATION TOPICS/SCHEDULE

Wed	**06.10.**	**Nb:**	**Toivonen**
Fri	**08.10.**	**Mo:**	**Ahmed, Shamshad**
Mon	**11.10.**	**Mn:**	**Majaniemi, Thakur, Ahkiola**
		Ru:	**Ichanson, Locqueville, Olsio**
We	**03.10.**	**Co:**	**Ekholm, Olander, Syväniemi**
		Cu:	**Kolawole, Nguyen, Munib**
Fri	**15.10.**	**In:**	**Kovanen, Ogunyemi, Svinhufvud**
		Te:	**Huhtakangas, Wallin, Kaarne**
Mon	**08.10.**	**Eu:**	**Sonphasit, Tuisku**
		Nd:	**Jussila, Siuro, Perttu**
		U:	**Sinkkonen, Wennberg, Partanen**

QUESTIONS: Lecture 13

- **Select two examples of critical elements, and describe why the element is critical, and how you think would be the best way to mitigate the criticality.**

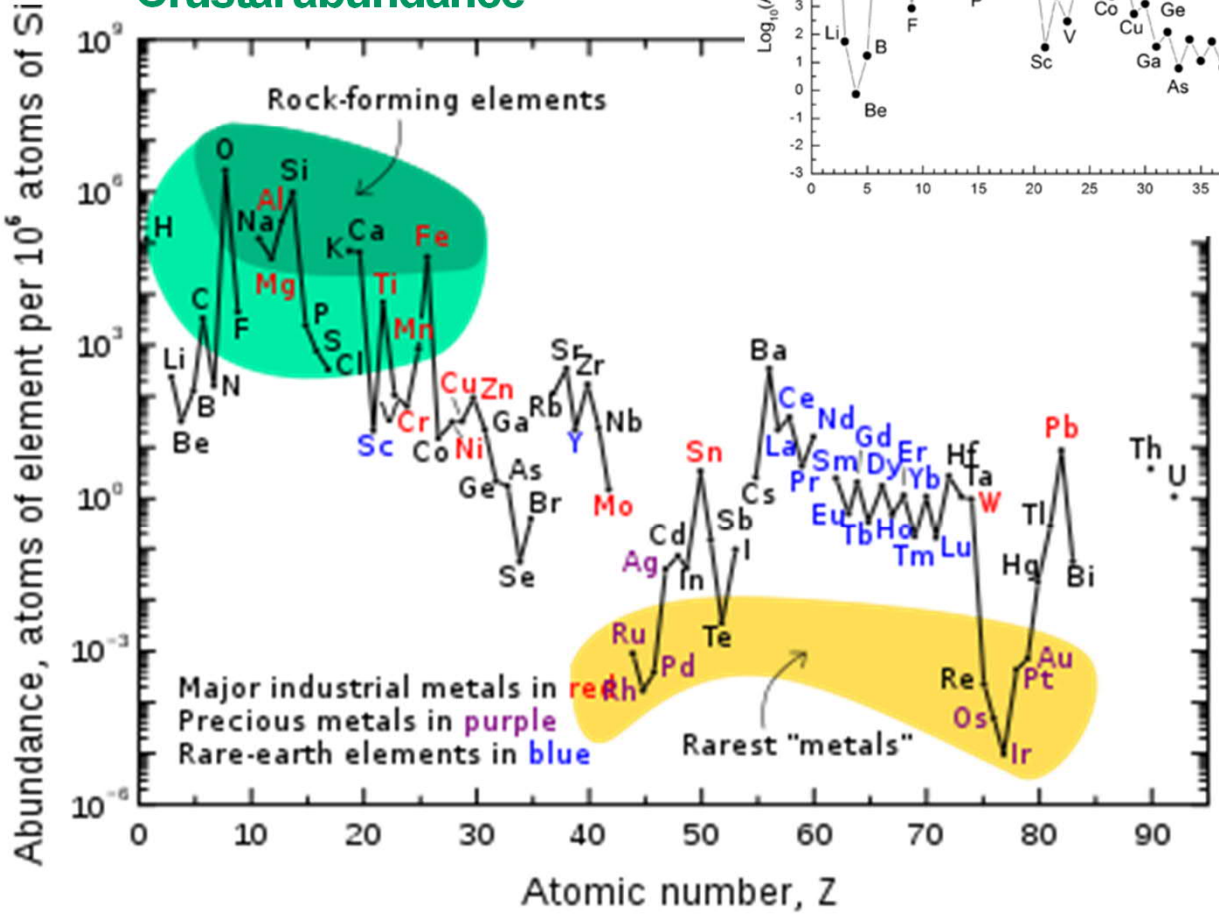
WHAT MAKES US CALL ELEMENTS RARE

- **Absolute abundance ?**
- **Accessable resources** (distribution, technical skills, etc.) ?
- **Availability** (politics, etc.) ?

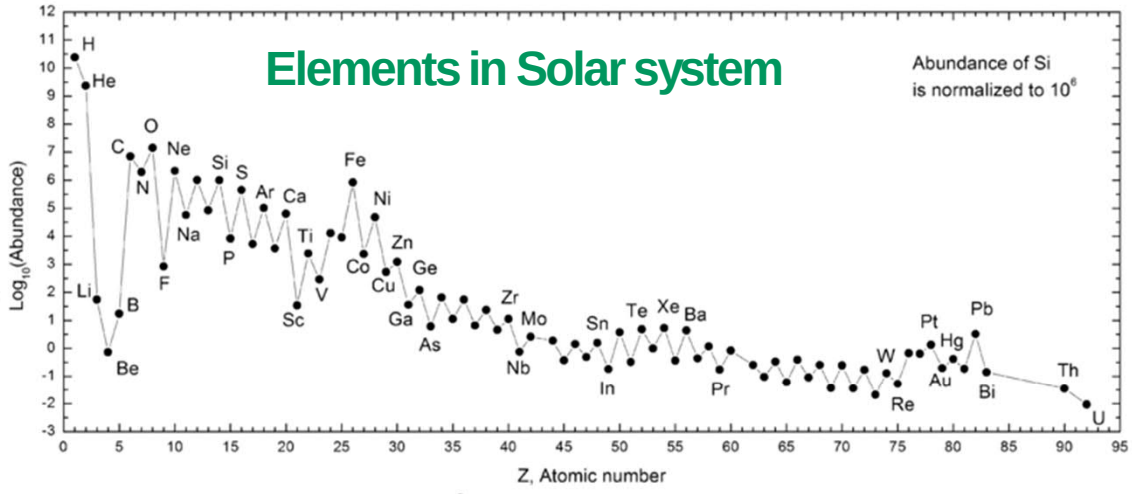
WHAT MAKES US CALL ELEMENTS CRITICAL

- **Essential to human health ?**
- **Needed to make crucial/desired devices ?**
- **Needed to generate/store energy ?**
- **Needed but not readily available ?**

Crustal abundance



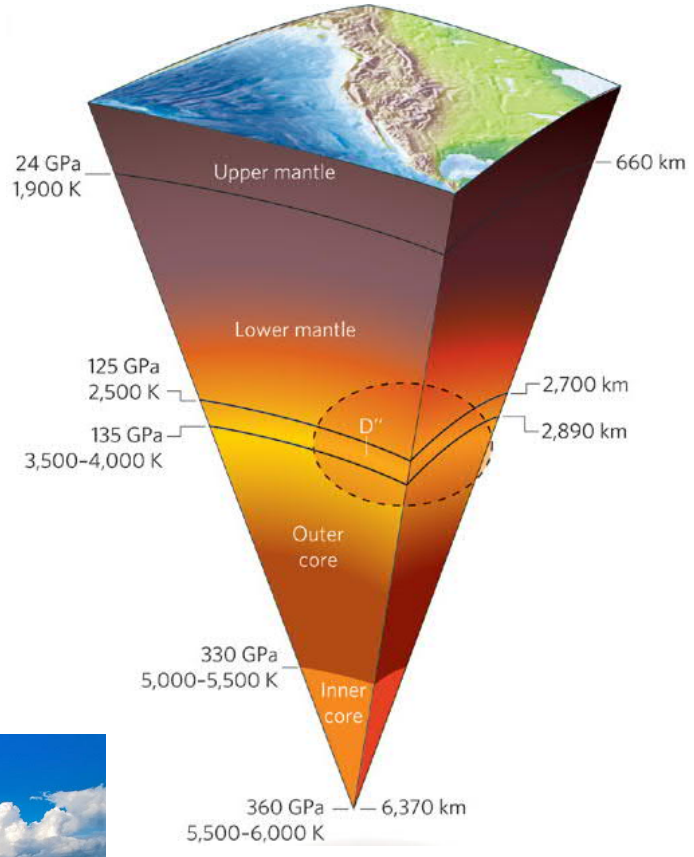
Elements in Solar system



ABSOLUTE ABUNDANCE

ACCESSABLE RESOURCES

- **Distribution of the elements**
- **Mining/separation technologies**
- ***Mponeng gold* mine in South Africa is the deepest mine in the world at a depth of ca. 4 km**



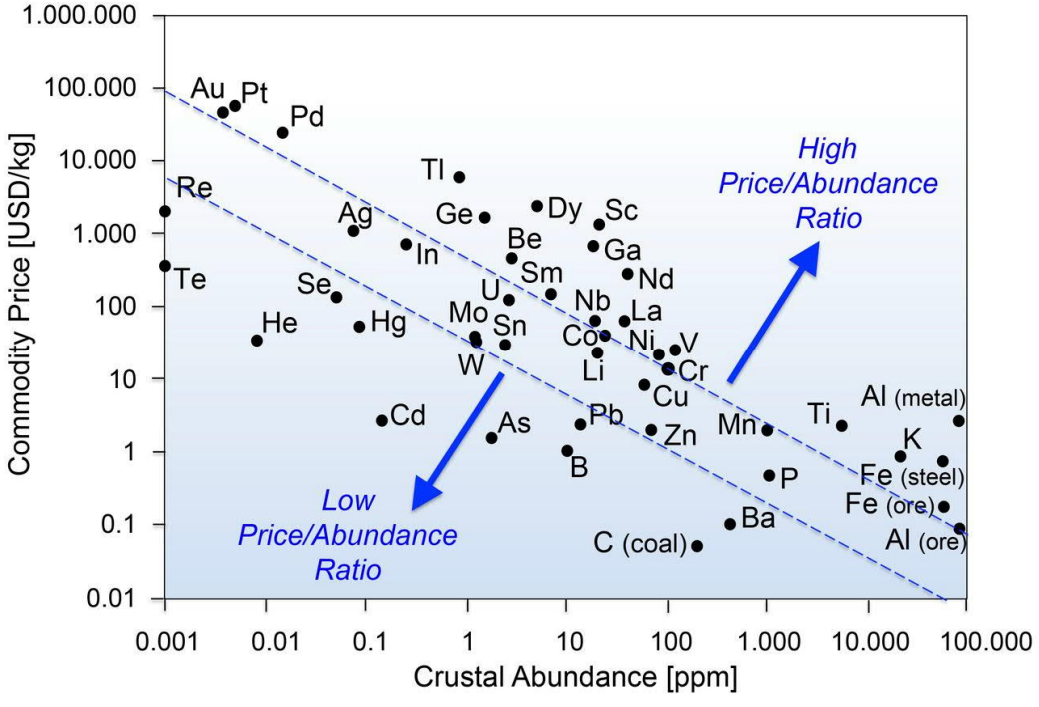
London metal exchange

	Official price
Aluminium	1,454.00
Aluminium Alloy	1,585.00
NASAAC	1,708.00
Copper	4,669.00
Lead	1,573.50
Nickel	8,955.00
Tin	14,660.00
Zinc	1,511.50
Cobalt	24,000.00
Molybdenum	10,800.00
Steel Billet	220.00

New York metal exchange

Top 10 Metals Products | Precious | Base | Ferrous | Other

Clearing	CME Globex	Floor	CME ClearPort	Product Name	Sub Group	Exchange	Volume	Open Interest
GC	GC	-	GC	Gold Futures	Precious	COMEX	187,052	428,212
SI	SI	-	SI	Silver Futures	Precious	COMEX	63,572	172,527
OG	OG	OG	OG	Gold Options	Precious	COMEX	25,194	1,515,879
PL	PL	-	PL	Platinum Futures	Precious	NYMEX	14,805	75,822
SO	SO	SO	SO	Silver Options	Precious	COMEX	6,498	165,506
PA	PA	-	PA	Palladium Futures	Precious	NYMEX	6,257	28,558
MGC	MGC	-	-	E-micro Gold Futures	Precious	COMEX	2,038	2,116
GCK	GCK	-	GCK	Gold Kilo Futures	Precious	COMEX	544	17
SIL	SIL	-	SIL	1,000-oz. Silver Futures	Precious	COMEX	206	2,003
QO	QO	-	-	miNY Gold Futures	Precious	COMEX	180	1,396



The Price

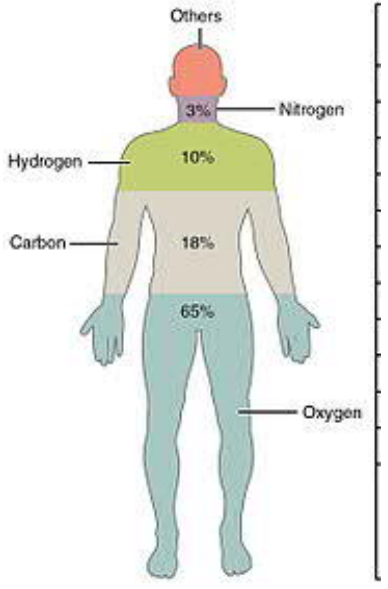
Price: affected by the rarity but also by fashion, speculation, politics, …

CRITICAL for Health & Wellbeing

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

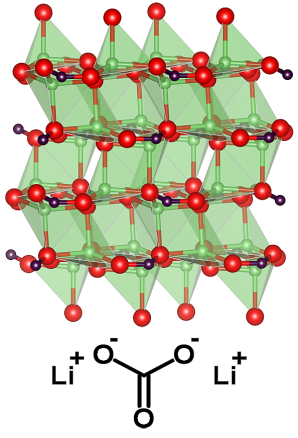
*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

The four organic basic elements | Quantity elements | Essential trace elements | Possible structural or functional role in mammals

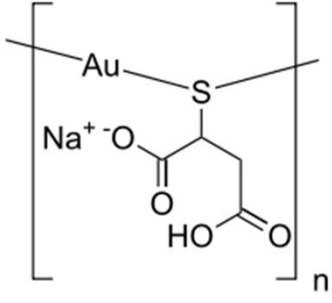


Supplement industry: $5 billion in sales

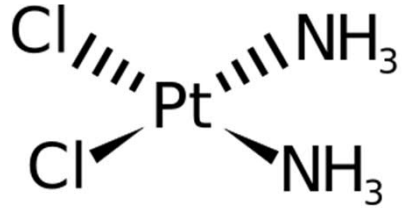
CRITICAL as MEDICINE



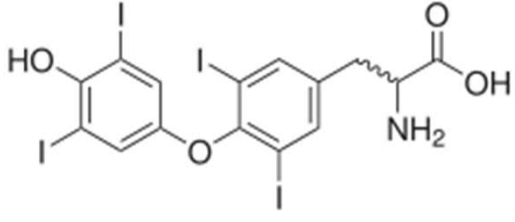
Li_2CO_3 for depression



Au for RA
(Rheumatoid Arthritis)



Cis-Pt complex for cancer



Iodine for thyroid hormones

Modern medicine relies not just on organics but often a range of elements

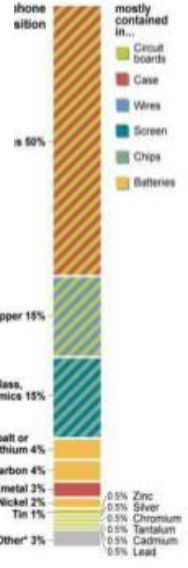
Almost the entire Periodic Table is being used ...

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Y	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	La	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ac	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U												

Elements used in the production of components for computers

CRITICAL for Modern Devices

Elements in a Mobile Phone



Source: Basel Convention, 2006; Lindholm (Nokia report), 2003

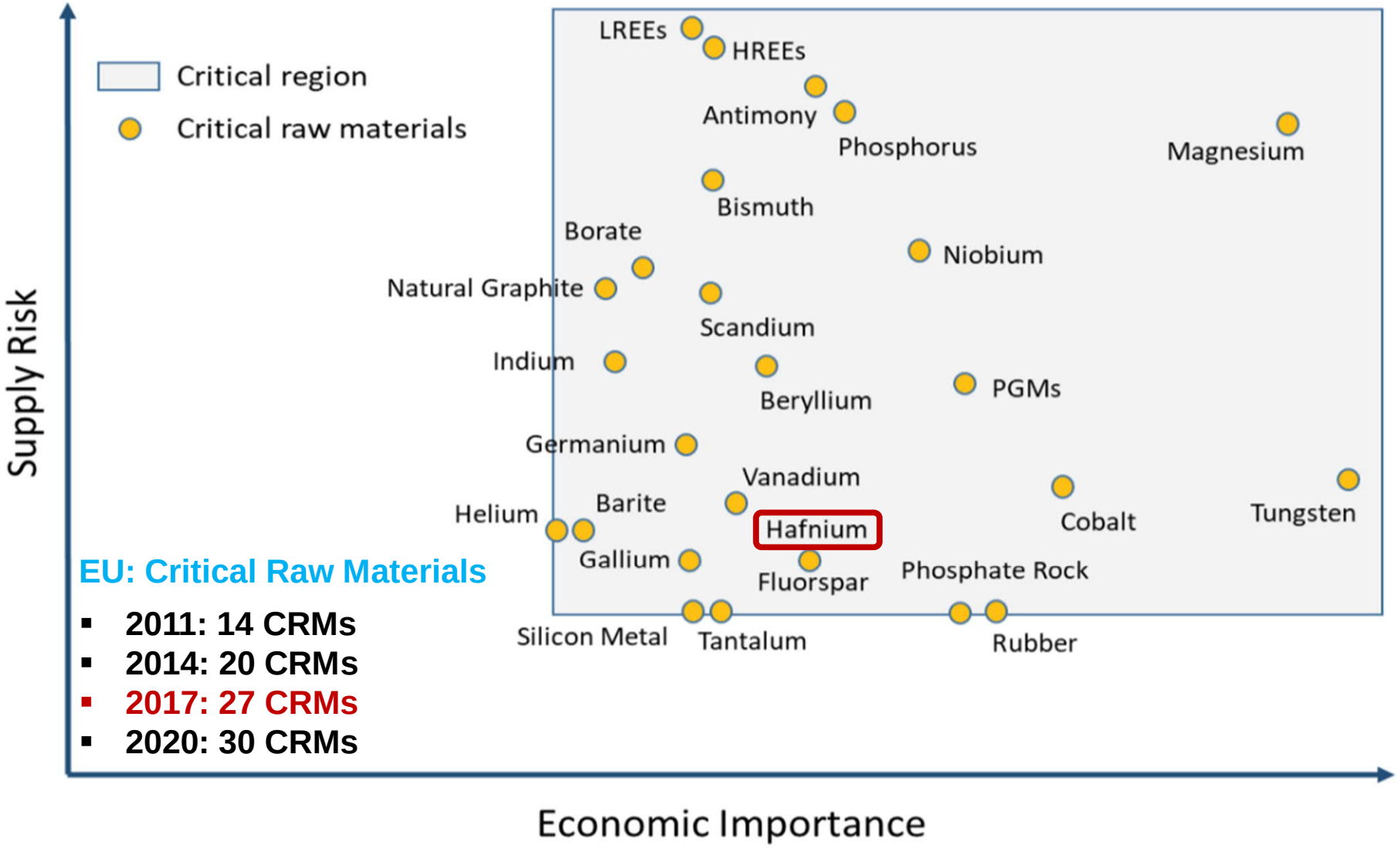
Roughly 40 different elements

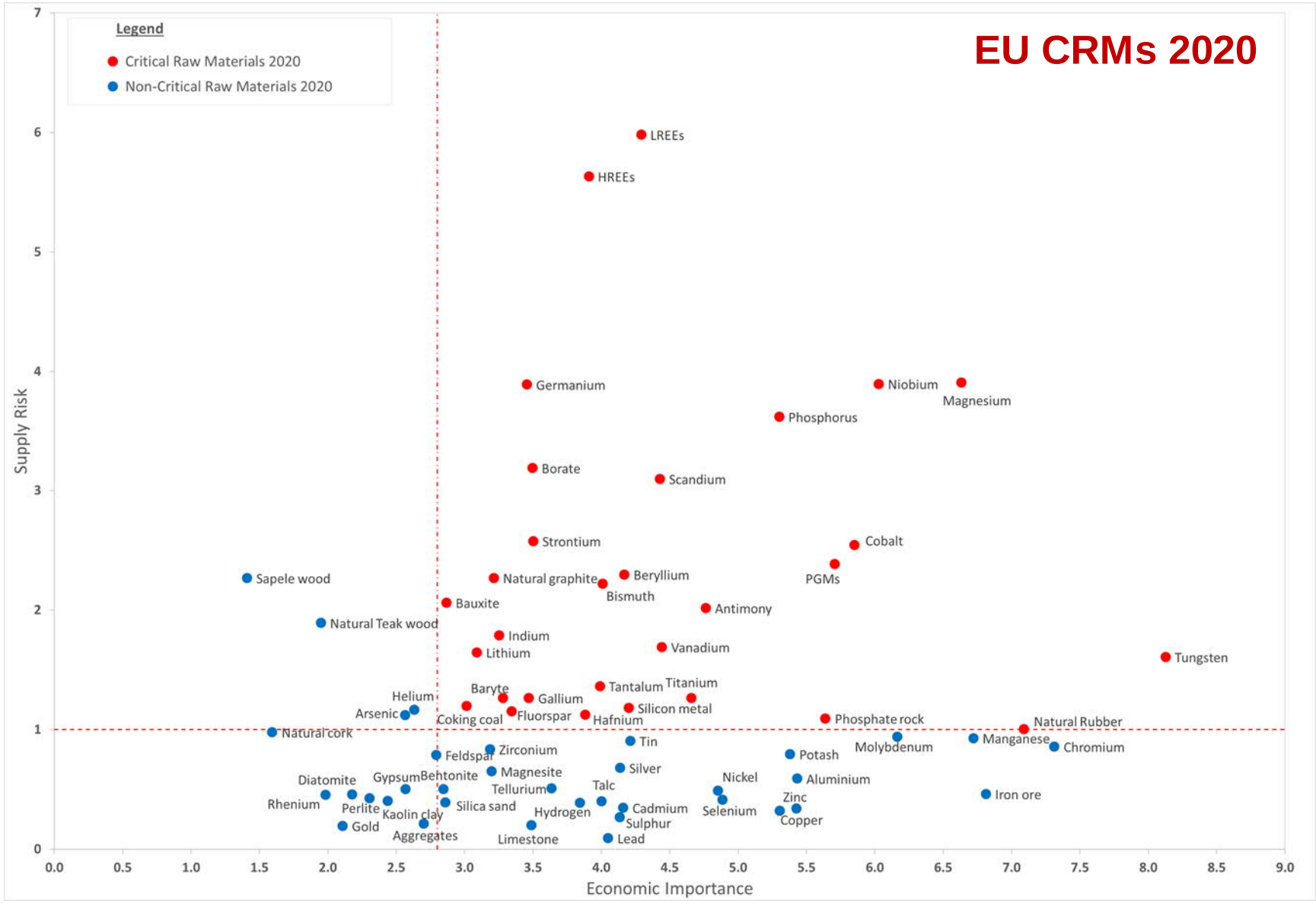
H, Li, Be, C, N, O, F, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Sr, Y, Zr, Ru, Pd, Ag, Cd, In, Sn, Sb, Ba, Ta, W, Pt, Au, Hg, Pb, Bi, Nd.

A mobile phone weighing 100 g contains:

- 13.7 g of copper
- 0.189 g of silver
- 0.028 g of gold
- 0.014 g of palladium

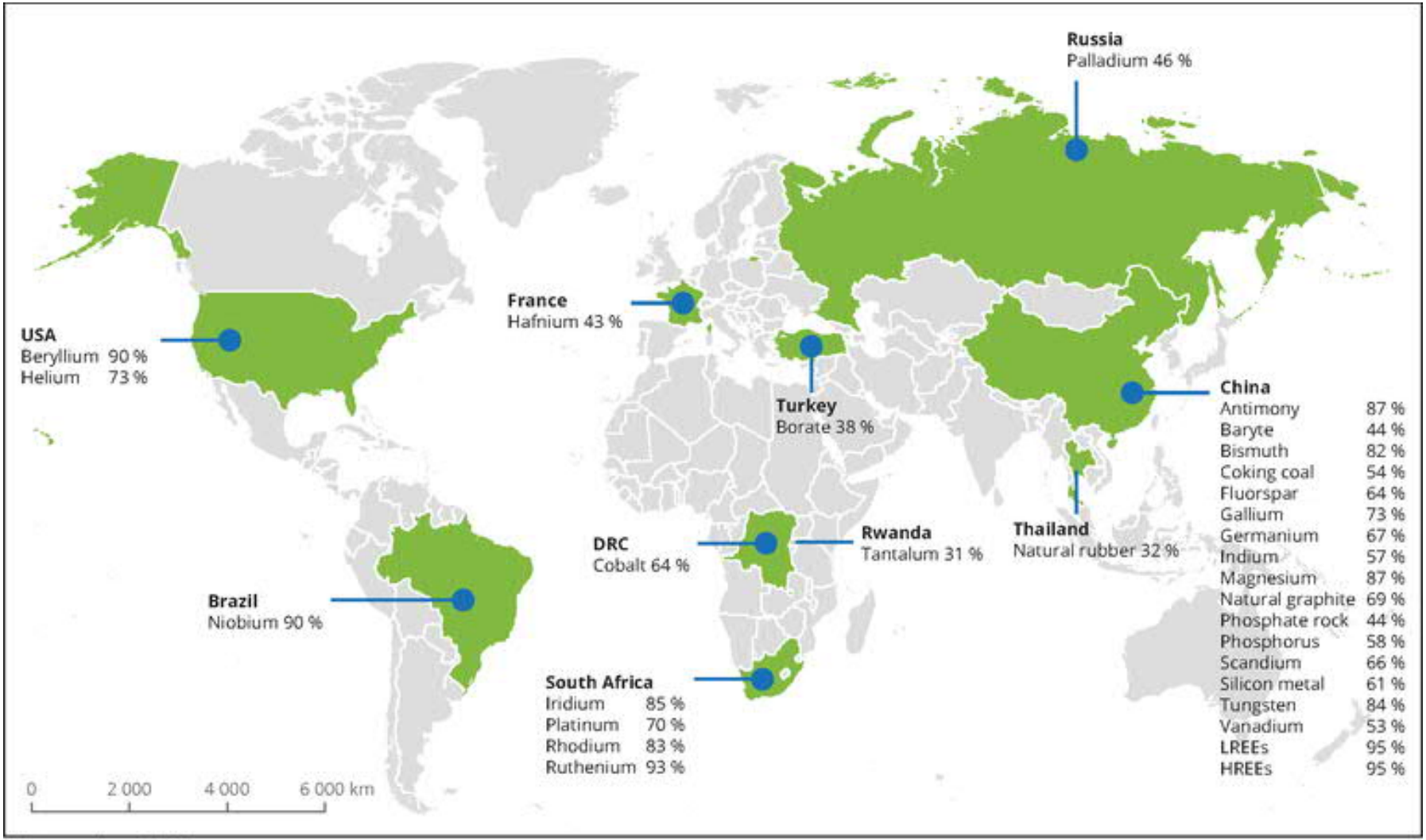
Courtesy of Dr Mike Pitts
Sustainability Manager


Critical region
Critical raw materials
Supply Risk
Economic Importance
LREEs
HREEs
Antimony
Phosphorus
Magnesium
Bismuth
Borate
Niobium
Natural Graphite
Scandium
Indium
Beryllium
PGMs
Germanium
Vanadium
Helium
Barite
Hafnium
Cobalt
Tungsten
Gallium
Fluorspar
Phosphate Rock
Silicon Metal
Tantalum
Rubber
EU: Critical Raw Materials
2011: 14 CRMs
2014: 20 CRMs
2017: 27 CRMs
2020: 30 CRMs


EU CRMs 2020
Legend
Critical Raw Materials 2020
Non-Critical Raw Materials 2020
Supply Risk
Economic Importance
LREEs
HREEs
Germanium
Niobium
Magnesium
Phosphorus
Borate
Scandium
Strontium
Cobalt
PGMs
Sapele wood
Natural graphite
Beryllium
Bismuth
Bauxite
Antimony
Natural Teak wood
Indium
Lithium
Vanadium
Tungsten
Baryte
Tantalum
Titanium
Helium
Gallium
Arsenic
Coking coal
Fluorspar
Hafnium
Silicon metal
Phosphate rock
Natural Rubber
Natural cork
Tin
Molybdenum
Manganese
Chromium
Feldspar
Zirconium
Potash
Silver
Diatomite
Gypsum
Bentonite
Magnesite
Nickel
Aluminium
Talc
Tellurium
Zinc
Iron ore
Rhenium
Perlite
Silica sand
Cadmium
Selenium
Copper
Kaolin clay
Hydrogen
Sulphur
Gold
Aggregates
Limestone
Lead

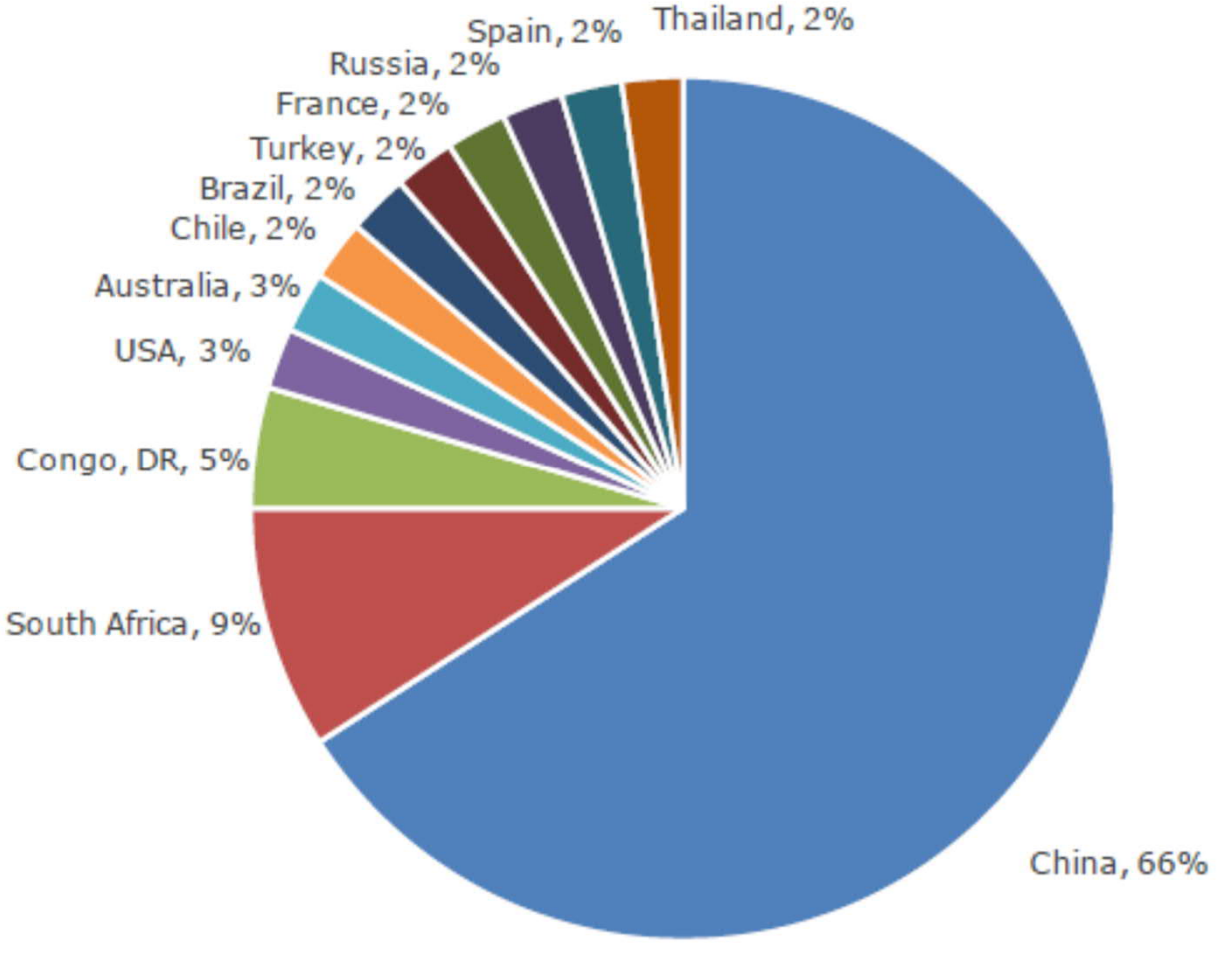
2020 Critical Raw Materials (new as compared to 2017 in bold)		
Antimony	Hafnium	Phosphorus
Baryte	Heavy Rare Earth Elements	Scandium
Beryllium	Light Rare Earth Elements	Silicon metal
Bismuth	Indium	Tantalum
Borate	Magnesium	Tungsten
Cobalt	Natural Graphite	Vanadium
Coking Coal	Natural Rubber	**Bauxite**
Fluorspar	Niobium	**Lithium**
Gallium	Platinum Group Metals	**Titanium**
Germanium	Phosphate rock	**Strontium**

WHICH COUNTRIES PRODUCE THE CRITICAL ELEMENTS/RAW MATERIALS ?



Reference data: ©ESRI

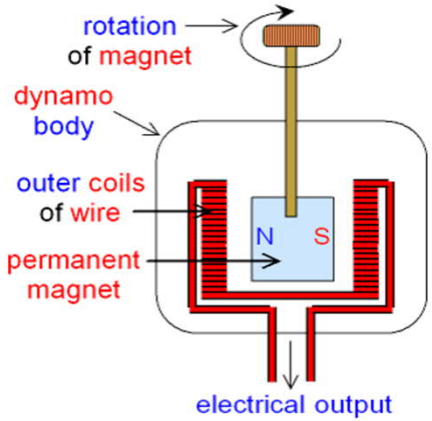
FROM WHICH COUNTRIES THE CRITICAL ELEMENTS/RAW MATERIALS COME TO EU CURRENTLY ?



MATERIALS for ENERGY

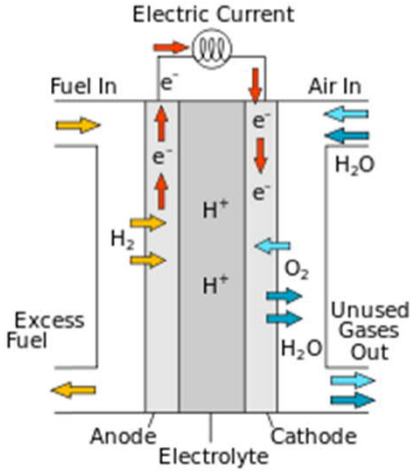
TURBINES: production of electricity from hydro, tidal, nuclear & fossil fuels

- REs (= Ln) for magnets
- (Cu), Ag, Au for wires



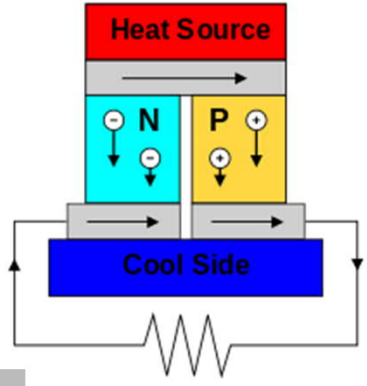
FUEL CELLS

- PEM: Pt, Pd; SOFC: Ni, Co, Ga, *Ln*



PHOTOVOLTAICS

- In, Ga, etc. …

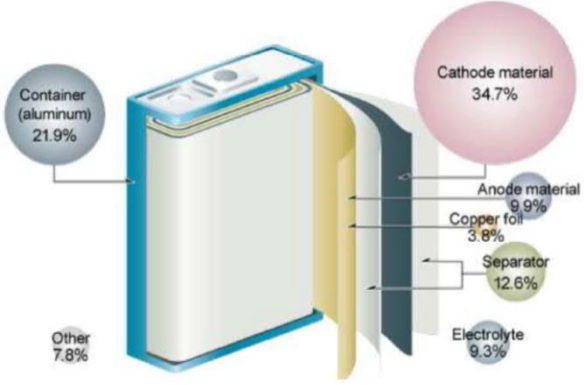


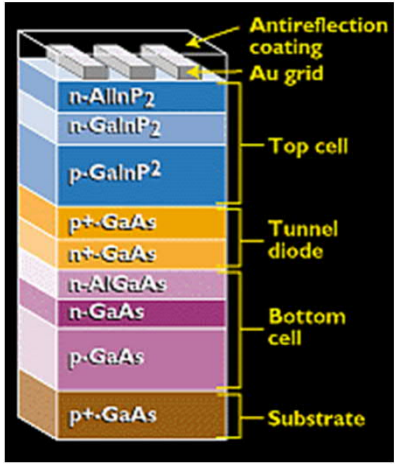
THERMOELECTRICS

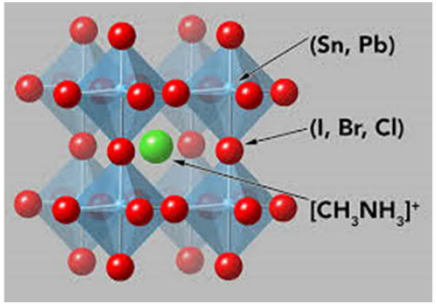
- Bi, Te, Se, Co, etc.

BATTERIES

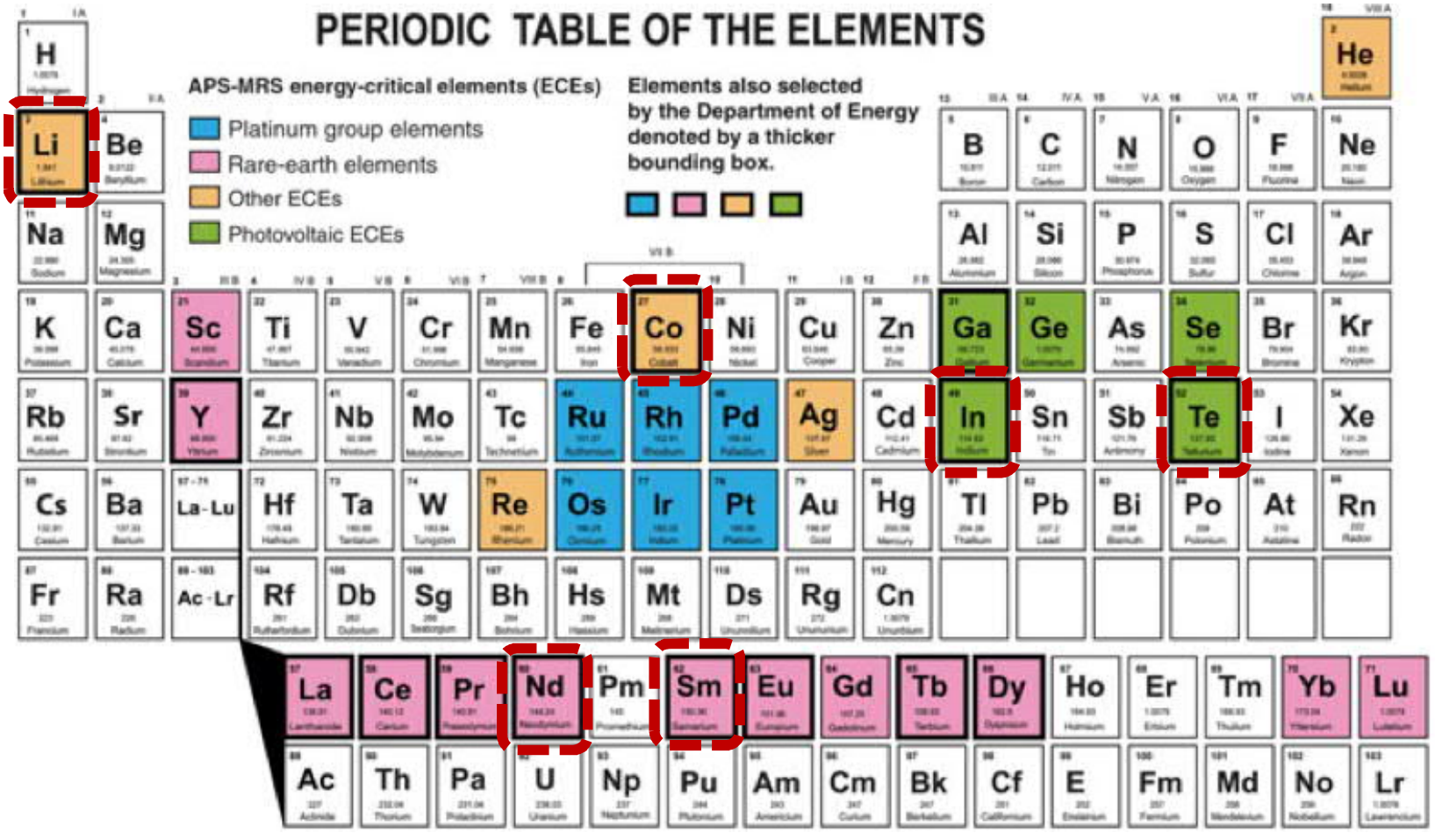
- Li, Co







ECE: Energy Critical Elements (by APS & MRS)



What should we do?

- RE-USE & RE-CYCLING

- SUBSTITUTING CRITICAL BY NON_CRITICAL

CONTRIBUTION of RECYCLING: TOO SMALL !

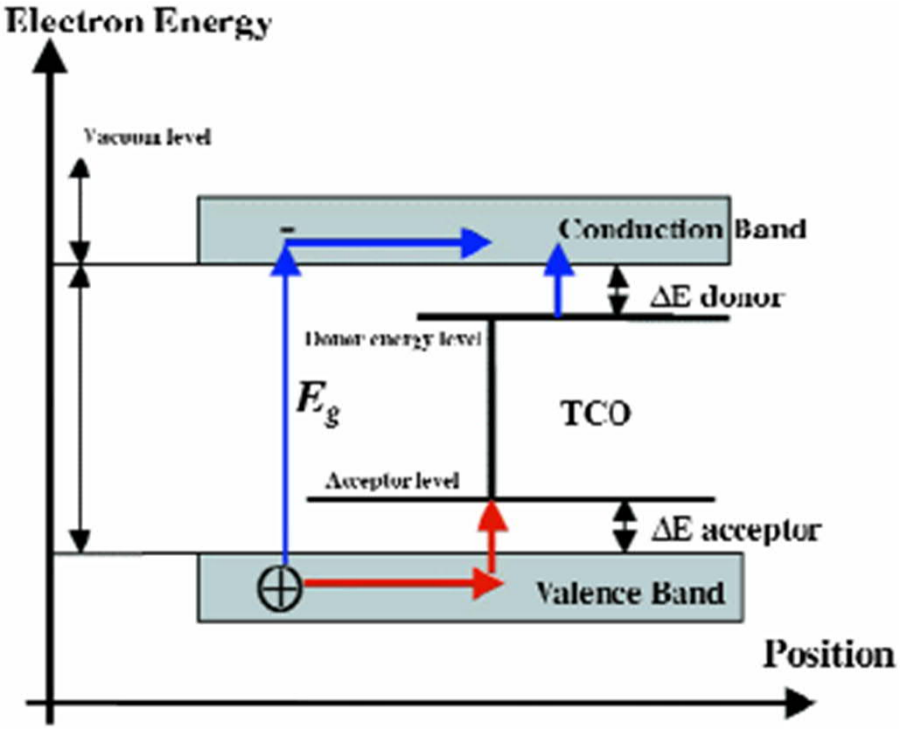
End-of-life recycling input rate (EOL-RIR) [%]

H																He 1%
Li 0%	Be 0%											B* 0.6%	C	N	O	F* 1%	Ne
Na	Mg 13%											Al 12%	Si 0%	P* 17%	S 5%	Cl	Ar
K* 0%	Ca	Sc 0%	Ti 19%	V 44%	Cr 21%	Mn 12%	Fe 24%	Co 35%	Ni 34%	Cu 55%	Zn 31%	Ga 0%	Ge 2%	As	Se 1%	Br	Kr
Rb	Sr	Y 31%	Zr	Nb 0%	Mo 30%	Tc	Ru 11%	Rh 9%	Pd 9%	Ag 55%	Cd	In 0%	Sn 32%	Sb 28%	Te 1%	I	Xe
Cs	Ba 1%	La-Lu[1]	Hf 1%	Ta 1%	W 42%	Re 50%	Os	Ir 14%	Pt 11%	Au 20%	Hg	Tl	Pb 75%	Bi 1%	Po	At	Rn
Fr	Ra	Ac-Lr[2]	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

> 50%
> 25-50%
> 10-25%
1-10%
< 1%

[1]Group of Lanthanide	La 1%	Ce 1%	Pr 10%	Nd 1%	Pm	Sm 1%	Eu 38%	Gd 1%	Tb 22%	Dy 0%	Ho 1%	Er 0%	Tm 1%	Yb 1%	Lu 1%
[2]Group of Actinide	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

SUBSTITUTIONS !?



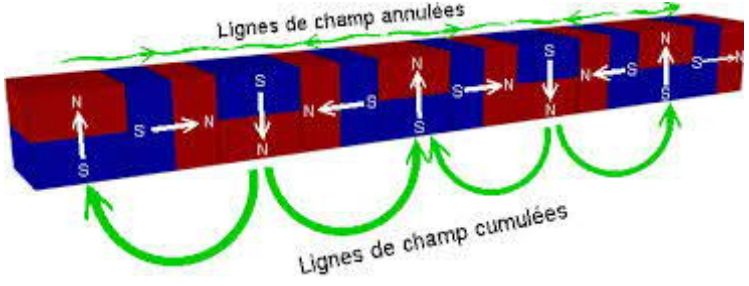
TRANSPARENT CONDUCTING OXIDES (TCOs)

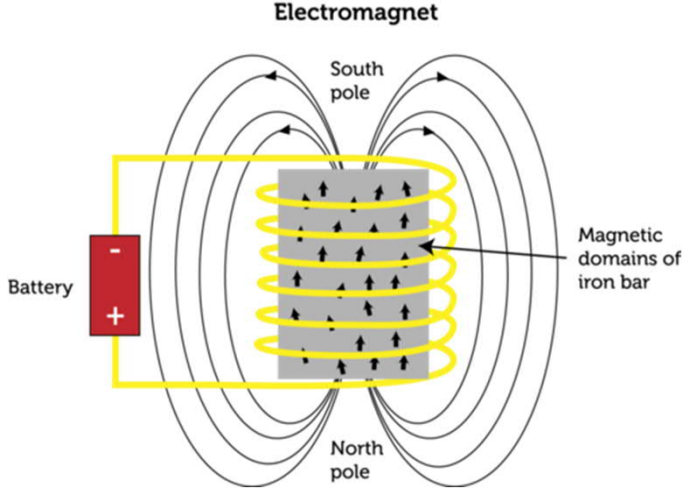
- **ITO (In-Sn-O) is the current commercial leader, but the waste recovery is very much limited**
- **F-doped SnO_2 is a good candidate**
- **Al-doped ZnO would be a highly sustainable replacement**

Strongest permanent magnet: $Nd_2Fe_{14}B$

"Non-Critical" ALTERNATIVES – Are there such ?

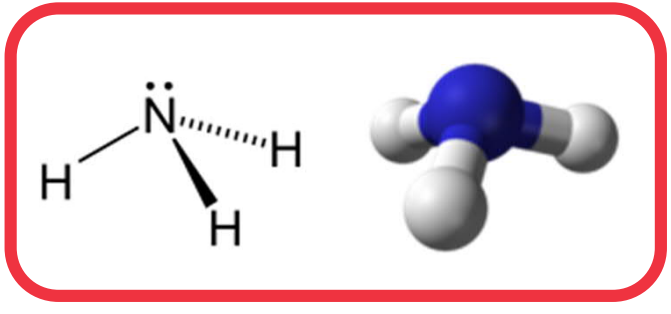
- **AlNiCo: "best of the rest"**
- **"Engineered" Fe_3O_4**
- **Electromagnets**

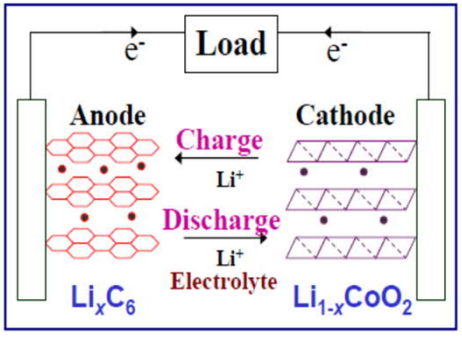




Elemental substitutions for toxicity

- $Ca^{2+} \rightarrow Cd^{2+}$: same size and charge
- K^{+} or $Ag^{+} \rightarrow Tl^{+}$: same size and charge
- $Bi^{3+} \rightarrow Pb^{2+}$: same stereo-active $6s^2$ electron pair





EC: ethylene carbonate

DEC: dimethyl carbonate

Li-ion battery

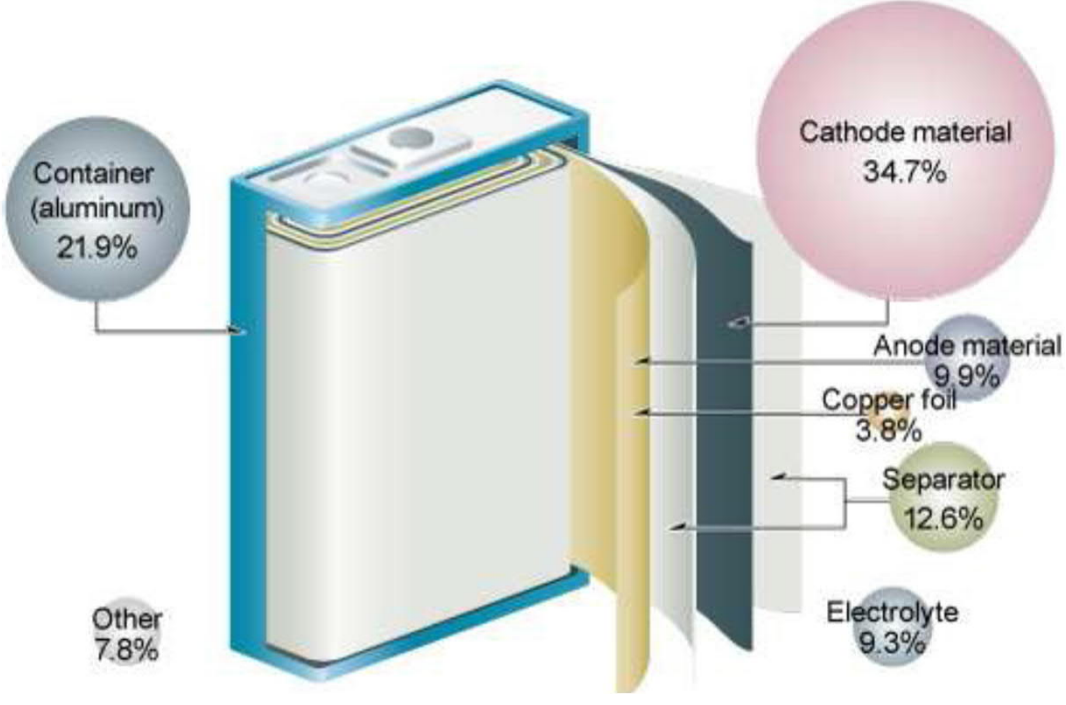
Cathode: $LiCoO_2$

Cell: (-) C | $LiPF_6$-(EC+DEC) | $LiCoO_2$ (+)

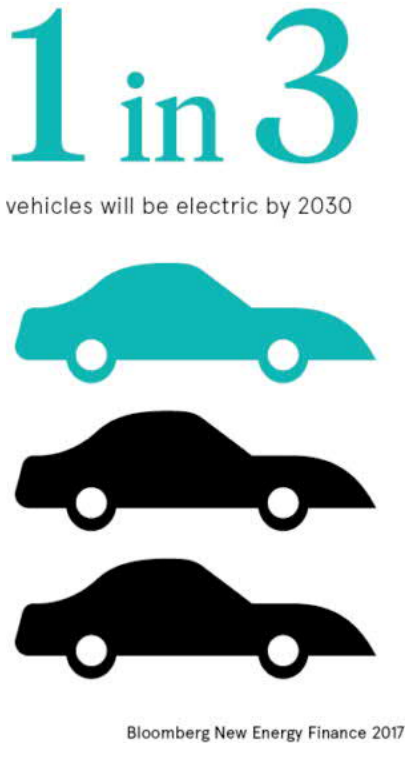
Cathode: $LiCoO_2 \underset{D}{\overset{C}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+ + xe^-$

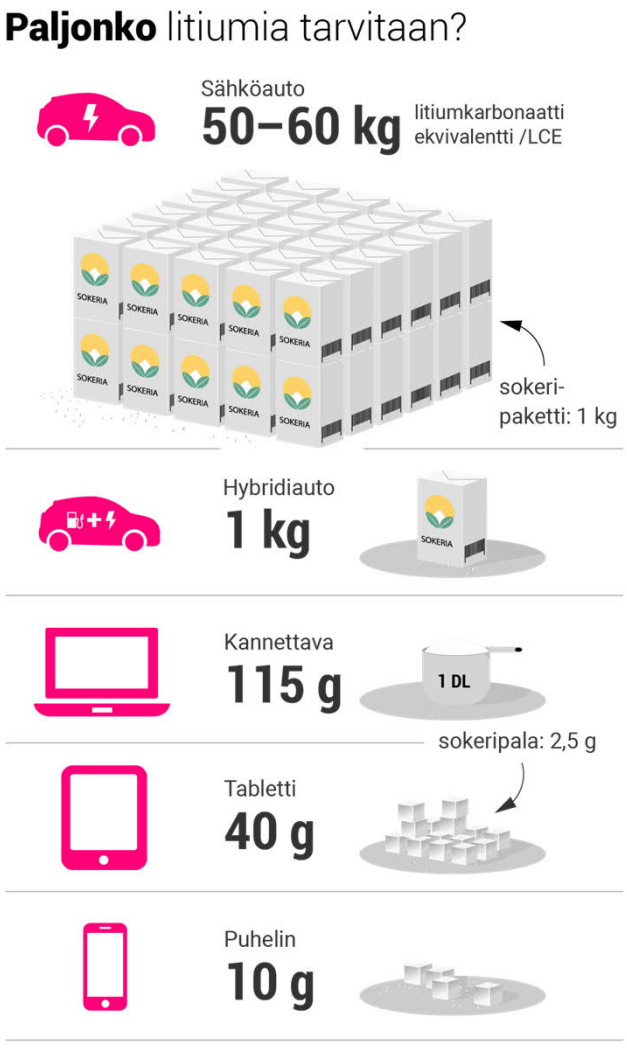
Anode: $6C + xLi^+ + xe^- \underset{D}{\overset{C}{\rightleftharpoons}} Li_xC_6$

Total: $LiCoO_2 + 6C \underset{D}{\overset{C}{\rightleftharpoons}} Li_{1-x}CoO_2 + Li_xC_6$



In 2030 one third of cars will be electric !





How much metals needed in 600 kg battery:

- 8 kg Li
- 7 kg Co
- 50 kg Ni

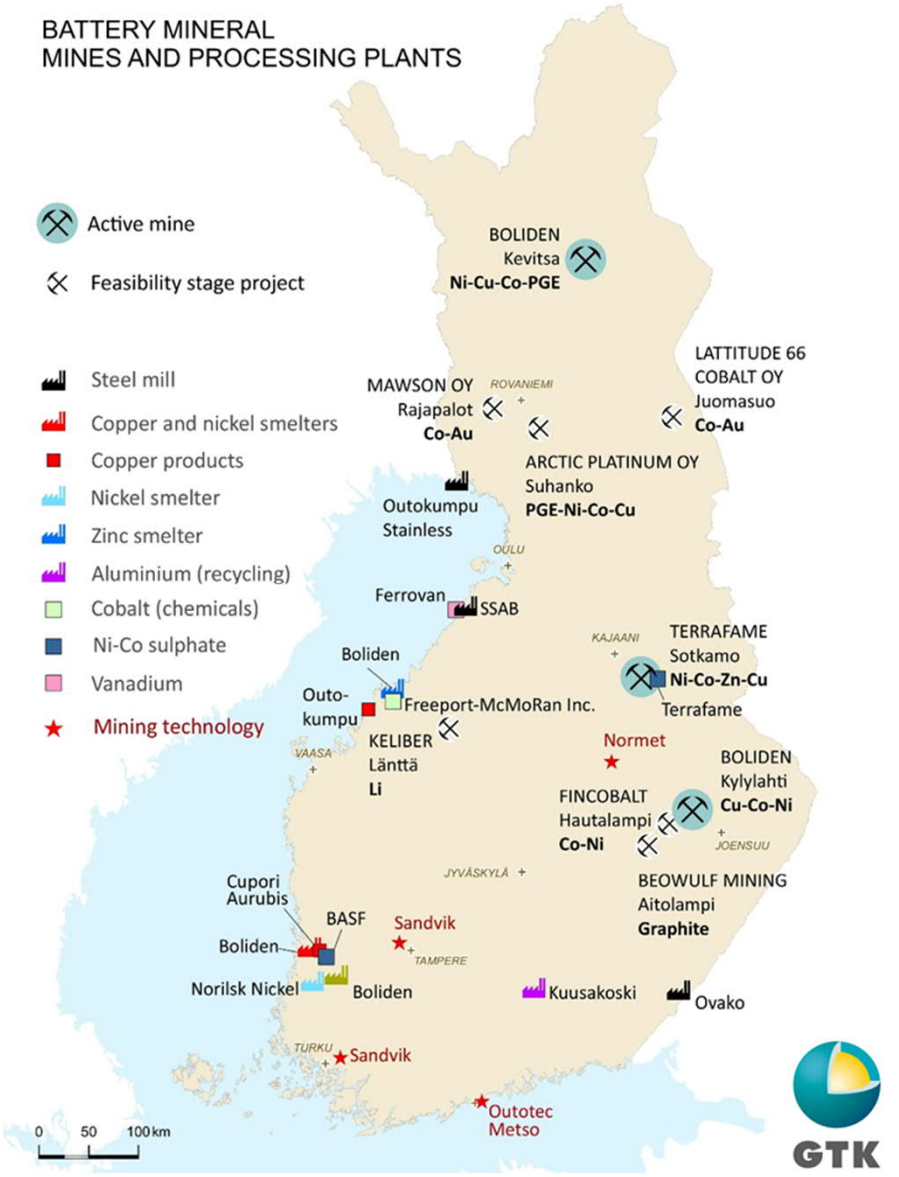
60 % of cobalt in the world is mined in Republic of Congo

Cobolt mining place in Congo close to Kasulo. Valokuvat: Siddharth Kara

Battery Minerals in FINLAND

- **Mining: Ni, Cu, Co**
- **Refining: Co (13 %), Ni, Cu**
- **Planned mining/refining: Li, Co (→ 2-4 %)**

“Ethical Cobalt/Metals”



Prof. Mari Lundström
Hydrometallurgy

Battery metals (Co, Li) from used batteries

Prof. Maarit Karppinen
Inorgaanic material chemistry

AALTO-CHEM COLLABORATION !

Performance of batteries made from recycled metals

Prof. Tanja Kallio
Electrochemistry

Electrode materials from recycled metals

C. Peng, K. Lahtinen, E. Medina, P. Kauranen, M. Karppinen, T. Kallio, B.P. Wilson & M. Lundström, Role of impurity copper in Li-ion battery recycling to $LiCoO_2$ cathode materials, *Journal of Power Sources* **450**, 227630 (2020).

CloseLoop (Closing the Loop for High-added-value Materials) supported by the STRATEGIC RESEARCH COUNCIL of FINLAND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BATCircle2.0

Consortium consists of:

- Aalto University, University of Eastern Finland, LUT University, University of Oulu
- Geological Survey of Finland (GTK), VTT Technical Research Centre of Finland
- Boliden Harjavalta Oy, Finnish Minerals Group Oy, Fortum Waste Solutions Oy, Metso Outotec Oyj, Norilsk Nickel Harjavalta Oy, Terrafame Oy, Umicore Finland Oy, AkkuSer Oy, BroadBit Batteries Oy, Oy Fennoscandian Resources Ab, FinnCobalt Oy, Keliber Technology Oy, Latitude 66 Cobalt Oy, Mawson Oy, X-Ray Minerals Services Finland Oy

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Finance & Markets

Finland to lead EU battery recycling research

It will cover the whole process starting from their collection and processing

By **Priyanka Shrestha**

Outotec tackling battery recycling with Aalto University and Business Finland

Posted by Paul Moore on 1st November 2018

The European Commission has invited Finland to coordinate the research related to recycling in the battery industry. Outotec will lead the project together with Aalto University's Department of Chemical and Metallurgical Engineering. Business Finland, a public research funding agency, is also strongly involved in advancing the project.

Outotec and Aalto University to coordinate European research related to recycling in the battery industry

Published: 01.11.2018

Company: **Outotec** Recommendation: **Lisää** Target price: **3.90 EUR** Share price: **3.74 EUR**

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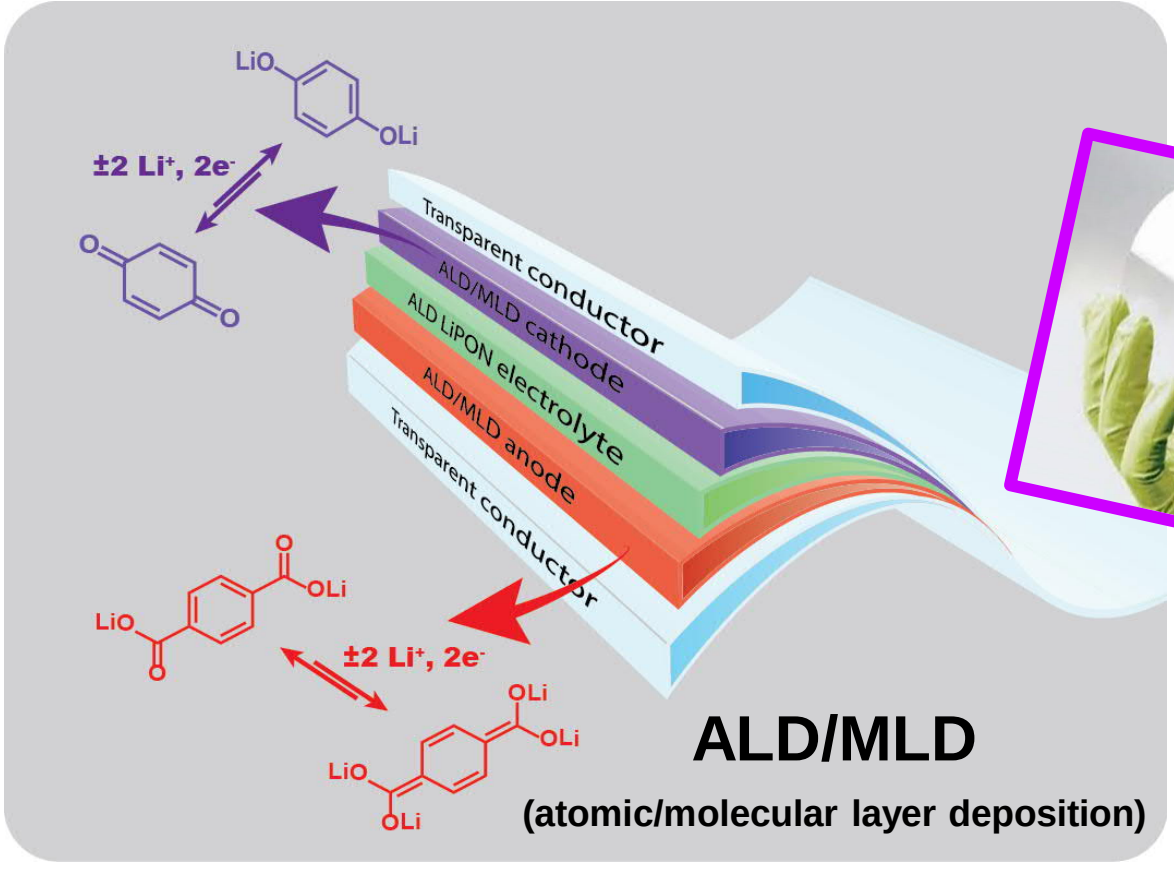
Outotec and Aalto University to coordinate European research related to recycling in the battery industry

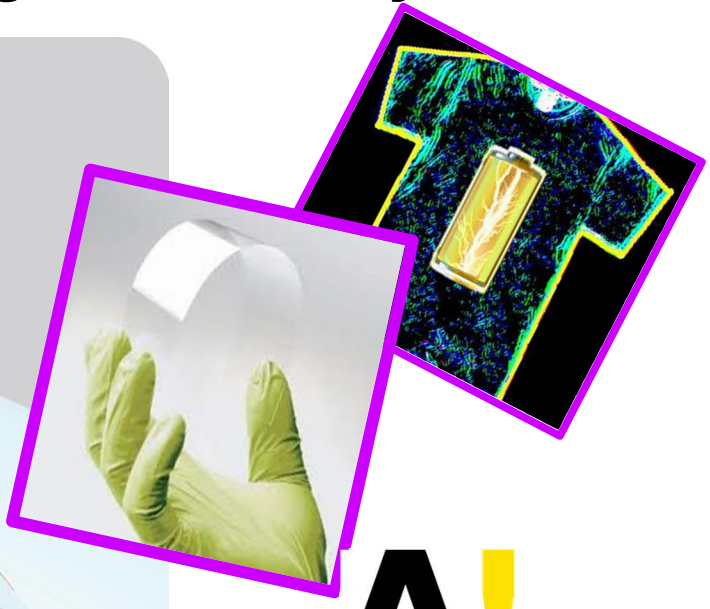
The European Commission has invited Finland to coordinate the research related to recycling in the battery industry. Outotec will lead the project together with Aalto University's Department of Chemical and Metallurgical Engineering. Business Finland, a public research funding agency, is also strongly involved in advancing the project.

Due to the rapidly growing demand for electric cars, the recycling of battery raw materials and equipment will become ever more important. The European Commission has compiled a

Key figures	2017	2018e	2019e
Turnover	1 143,8	1 335,4	1 430,4
Growth rate	8,1%	16,8%	7,1%
EBIT	26,0	-41,7	95,2
EBIT margin	2,3%	-3,1%	6,7%
Adjusted EPS	-0,03	0,19	0,30

Flexible safe “metal-sparing” Li-organic battery





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