LECTURE SCHEDULE

Mon (Ke3) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Ke5) 10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu & Magnetism
10.	Fri	29.09.	Cu & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Mon 25.09.	**Mo:**	**Maryam Jafarishiad & Saara Siekkinen**
Wed 27.09.	**Mn:**	**Naomi Lyle & Sanni Ilmaranta**
	Ru:	**Miklos Nemeszeghy & Timo de Jonge**
Fri 29.09.	**Cu:**	**Koshila Hiruni & Kaushalya Poonanoo**
Wed 04.10.	**Eu:**	**Binglu Wang & Mari Heikkinen**
	Nd:	**Patrich Wiesenfeldt & Tomoki Nakayama**
	U:	**Miikka Viirto & Ashish Singh**
Fri 06.10.	**Co:**	**Gabrielle Laurent & Yan Zheng**
	In:	**Sonja Alasaukko-oja & Katri Haapalinna**
	Te:	**Sofia Rantala & Roger Peltonen**

QUESTIONS: Lecture 13

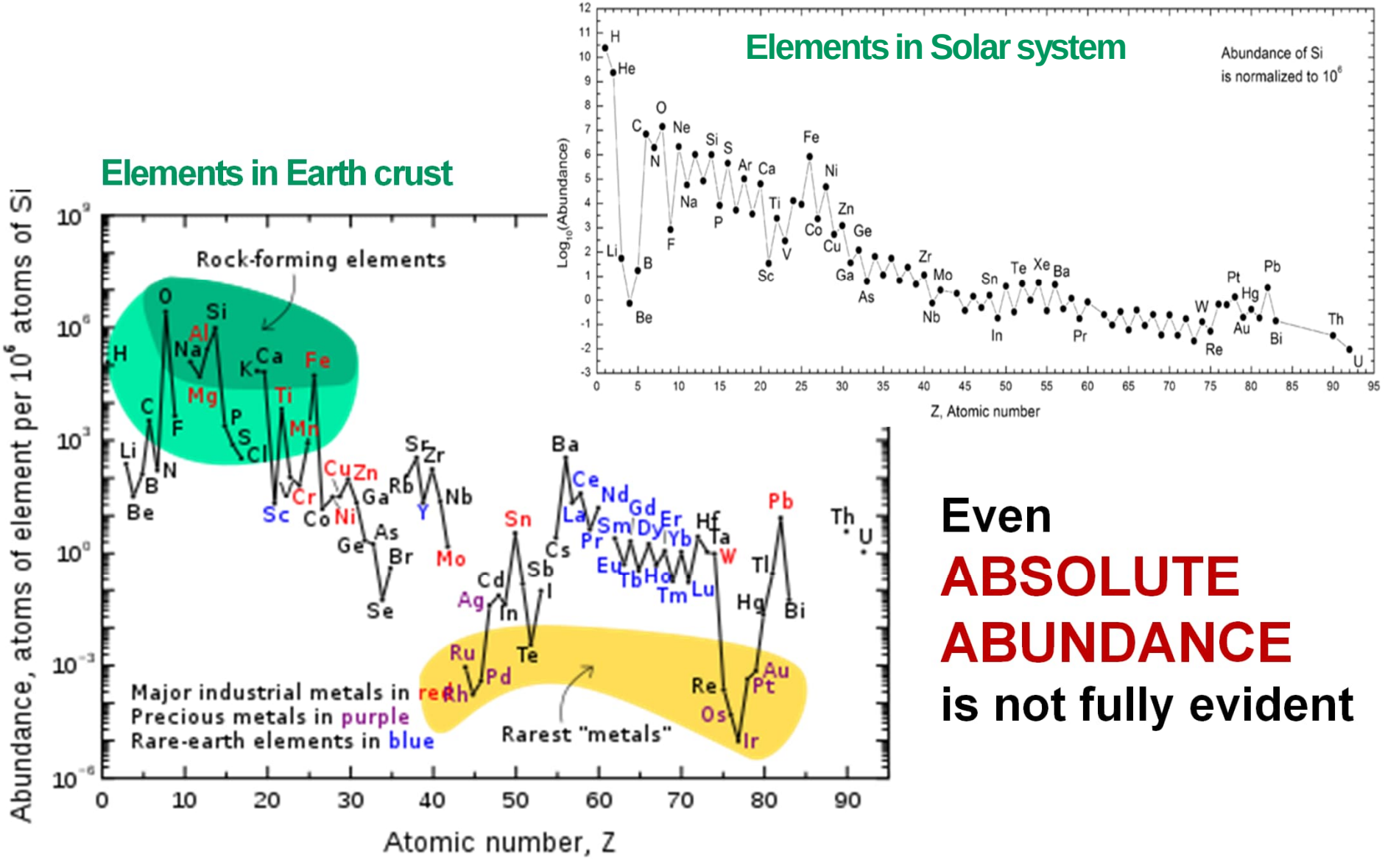
Select two examples of EU critical elements, and describe in each case why the element is critical, and how you think would be the best way to mitigate the criticality.

WHAT MAKES US CALL ELEMENTS RARE

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

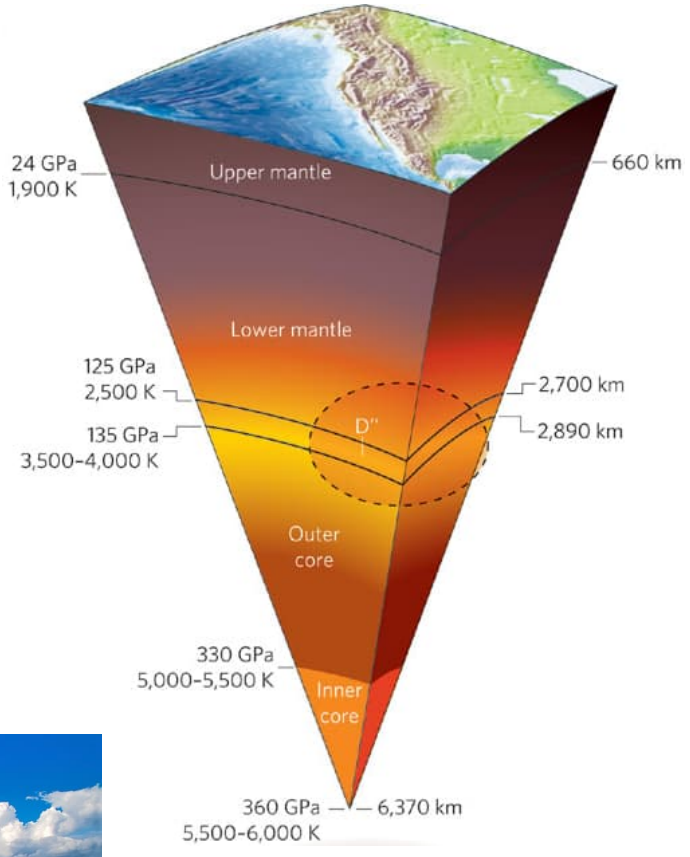
WHAT MAKES US CALL ELEMENTS CRITICAL

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


Elements in Solar system
Abundance of Si
is normalized to 10^6
Log10(Abundance)
Z, Atomic number
Elements in Earth crust
Rock-forming elements
Abundance, atoms of element per 10^6 atoms of Si
Atomic number, Z
Major industrial metals in red
Precious metals in purple
Rare-earth elements in blue
Rarest "metals"
Even
ABSOLUTE
ABUNDANCE
is not fully evident

ACCESSIBLE RESOURCES

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



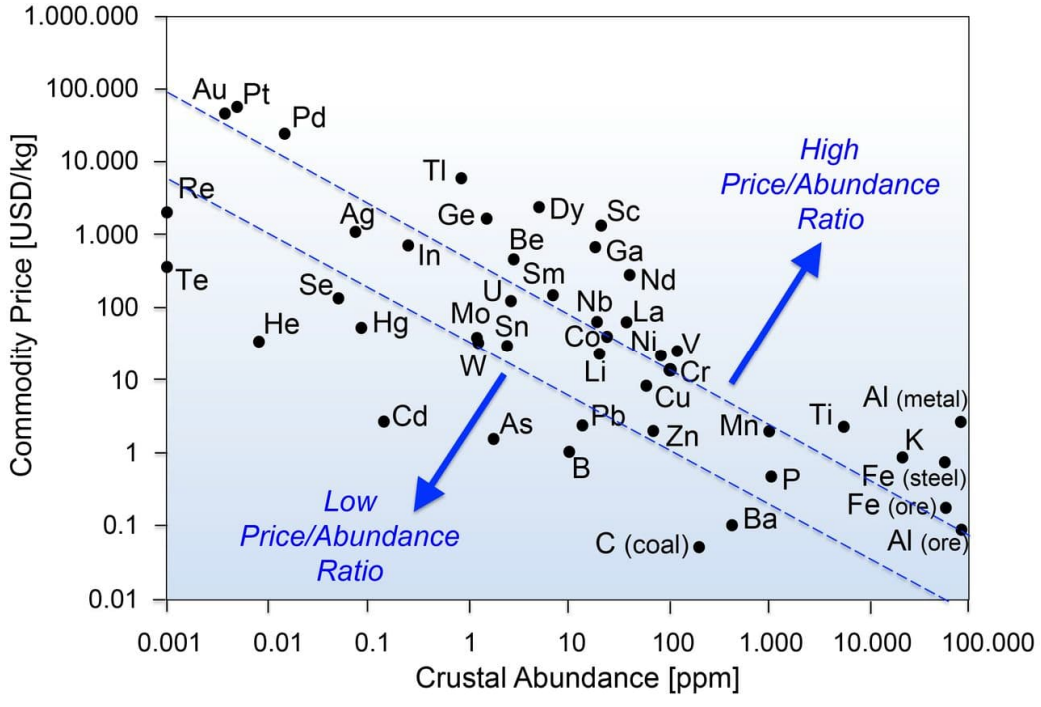
London metal exchange

	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 !

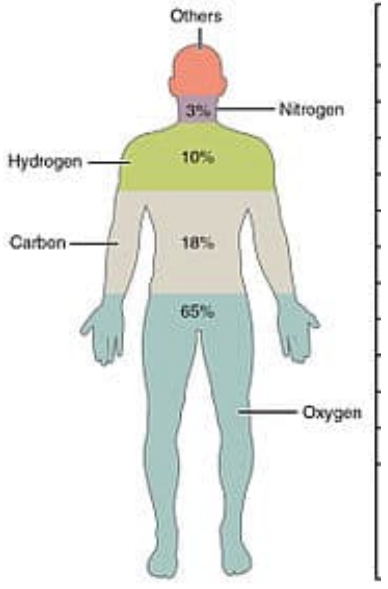
Price: affected by the rarity but also by fashion, speculation, politics, …

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

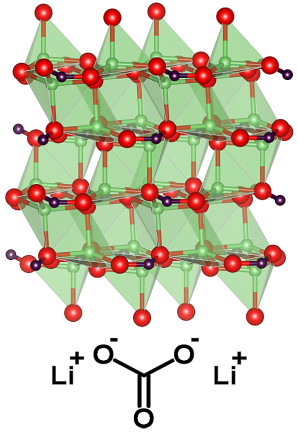
*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

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

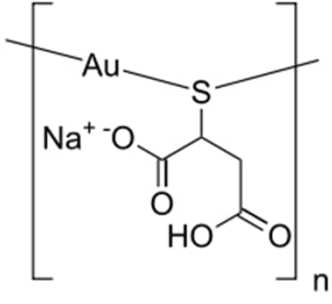


Supplement industry is huge business

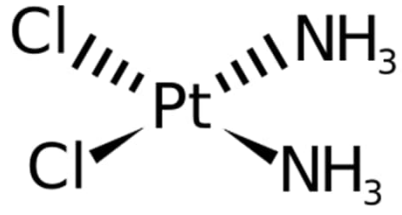
CRITICAL as MEDICINE



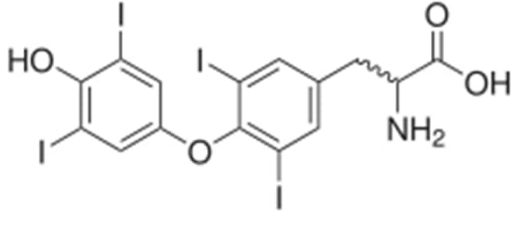
Li_2CO_3 for depression



Au for RA
(Rheumatoid Arthritis)



Cis-Pt complex for cancer



Iodine for thyroid hormones

Medicines are based not only on organics but on a much wider variety of elements

Almost the entire Periodic Table is being used …

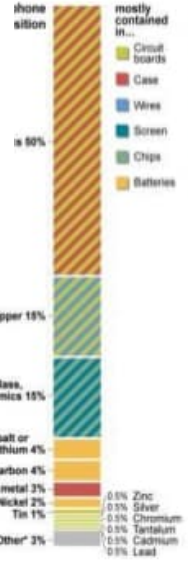
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Y	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	La	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ac	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																

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



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.

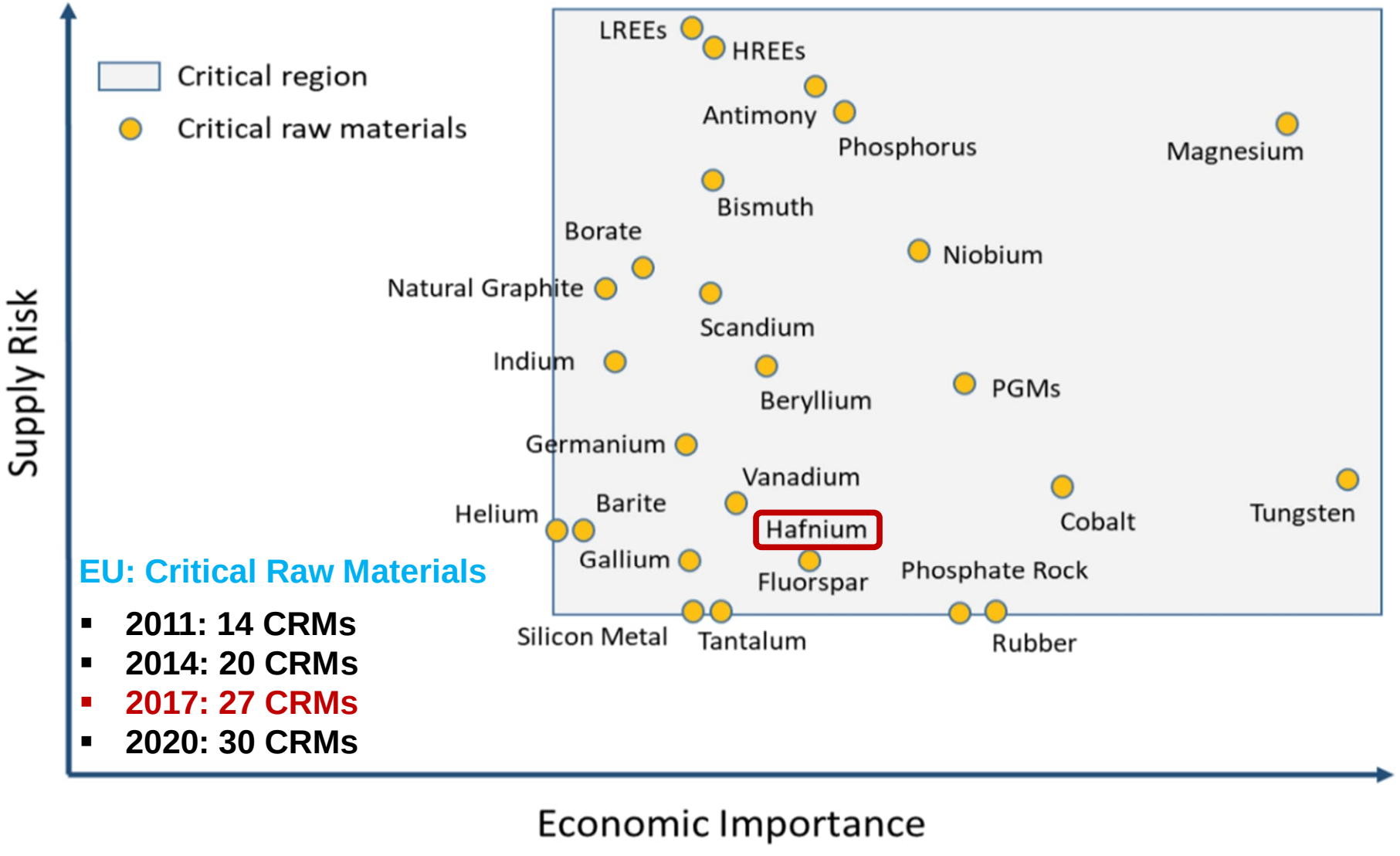
A mobile phone weighing 100 g contains:

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

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

Courtesy of Dr Mike Pitts
Sustainability Manager

https://rmis.jrc.ec.europa.eu/?page=crm-list-2020-e294f6



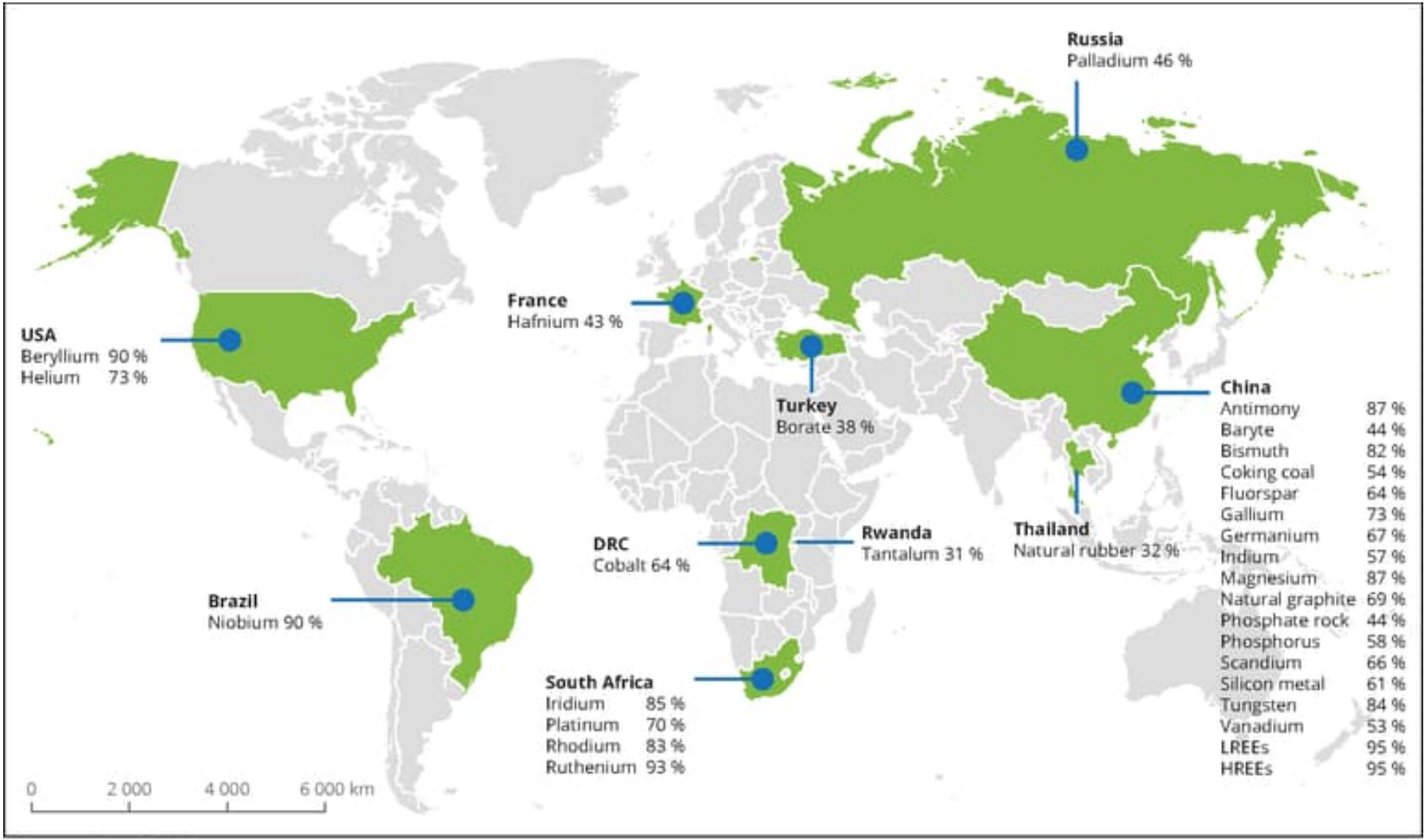
2023 Critical Raw Materials (*Strategic Raw Materials in italics*)			
aluminium/bauxite	coking coal	*lithium*	phosphorus
antimony	feldspar	*LREE*	scandium
arsenic	fluorspar	*magnesium*	*silicon metal*
baryte	*gallium*	*manganese*	strontium
beryllium	*germanium*	*natural graphite*	tantalum
bismuth	hafnium	niobium	*titanium metal*
boron/borate	helium	*PGM*	*tungsten*
cobalt	*HREE*	phosphate rock	vanadium
		*copper**	*nickel**

* Copper and nickel do not meet the CRM thresholds, but are included as Strategic Raw Materials.

Nickel, being a Strategic Raw material, is the only battery material which has never been on the list because of good supply diversification for the assessed period. Assessment however neither reflects the concentration of ownership of the projects and production capacities, nor private contractual arrangements, which may become an issue for the future. Main global producers of ores and concentrates are Indonesia 26%, Philippines 14%, Russia 10%, New Caledonia 9%, Canada 8%, Australia 8% and several smaller producers; and EU sources 39% from Finland, 24% from Canada, 19% from Greece, 8% from South Africa, 4% from the US. Main refiners are China 33%, Indonesia 12%, Japan 9%, Russia 7% and several smaller producers; EU sources refined nickel from 29% from Russia, 18% from Finland, 11% from Norway, 7% from Canada, 7% from Australia, 4% from Greece and several smaller importers.

Copper, being a Strategic Raw material, is used in very large quantities of 20 Mt in 2020 for electrification across all strategic technologies. Its supply is very well diversified, therefore it has not been considered critical before. However, it is challenging to substitute due to its superior performance in electrical applications.

WHICH COUNTRIES PRODUCE THE CRM METALS (2020) ?



Reference data: ©ESRI

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

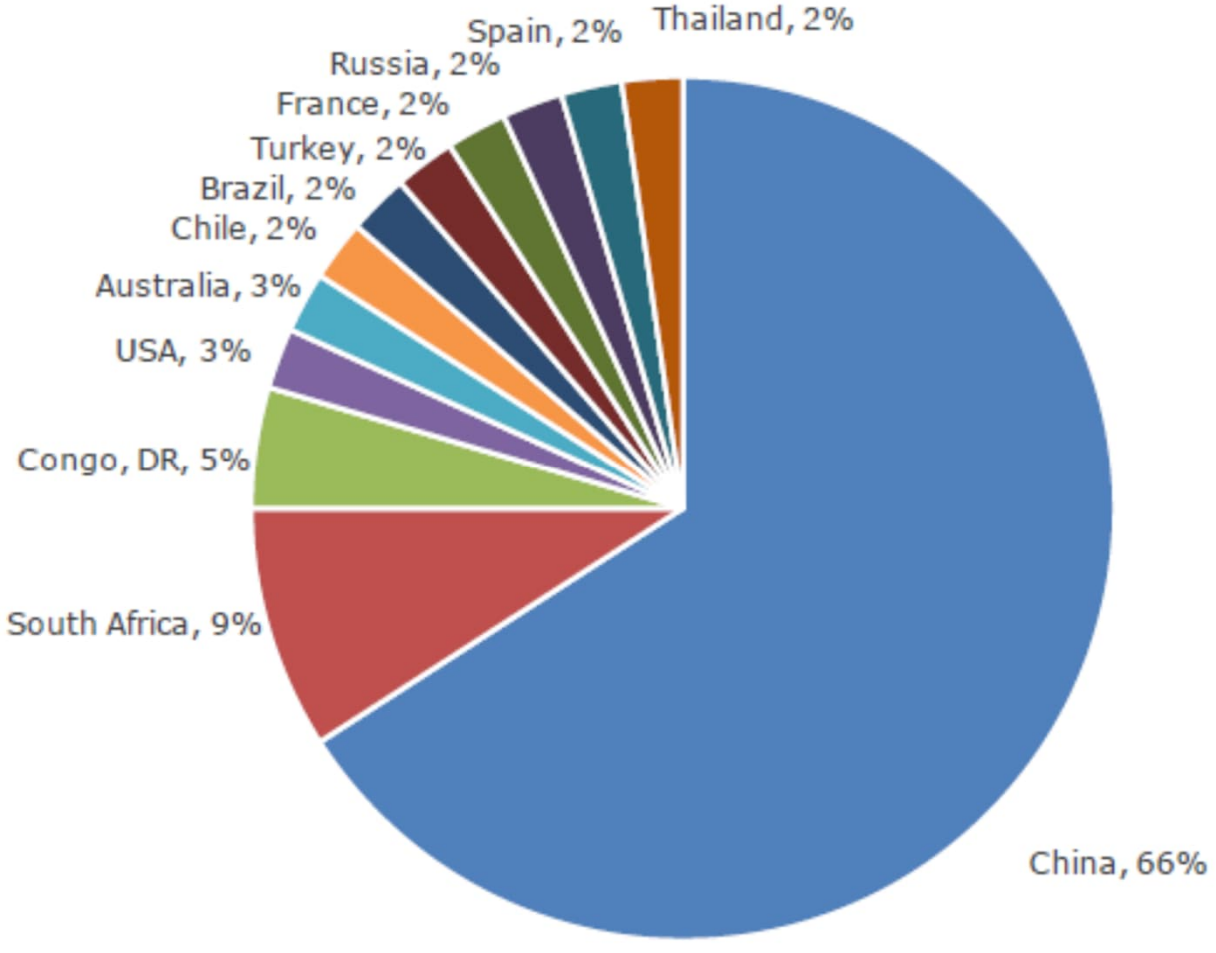
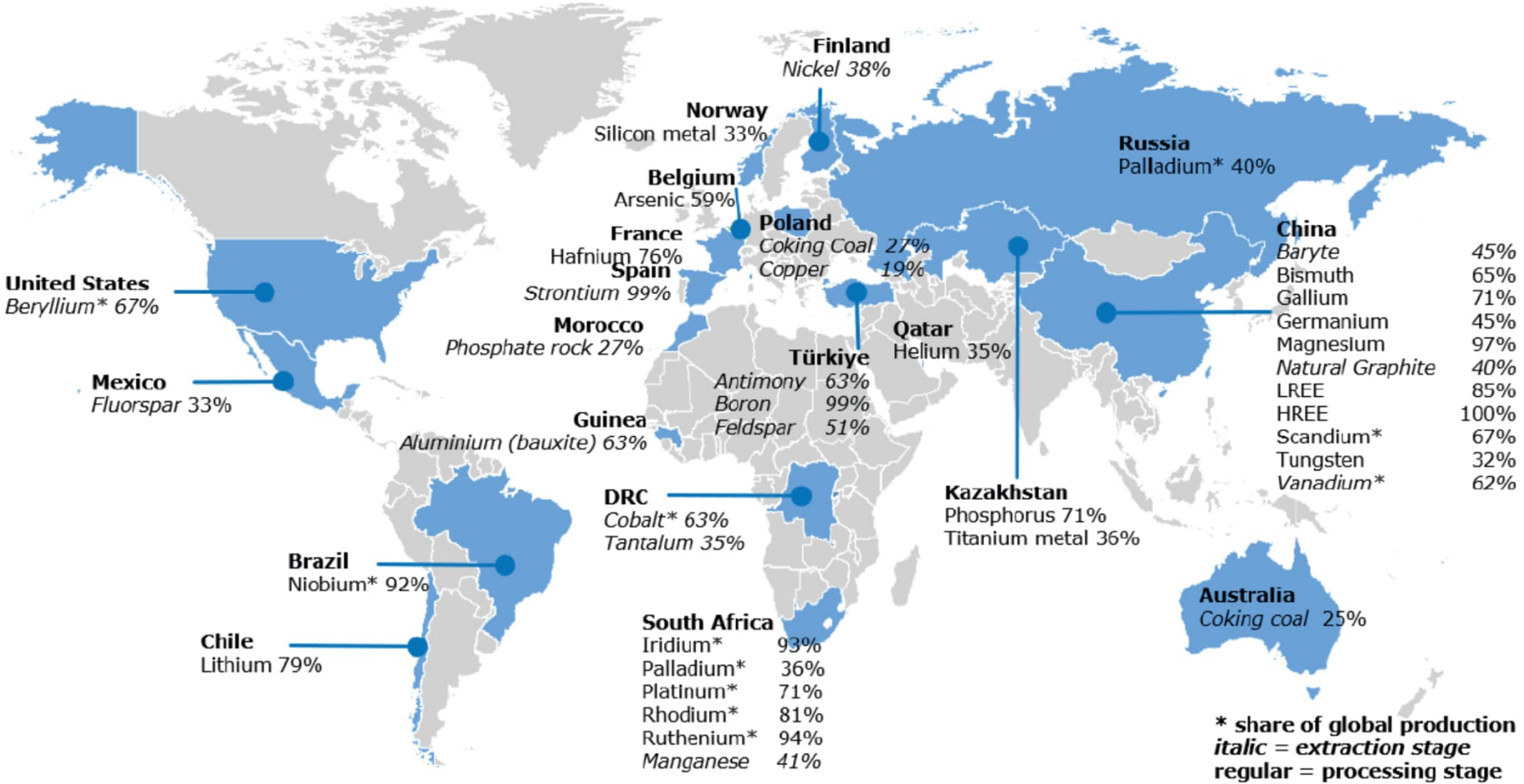
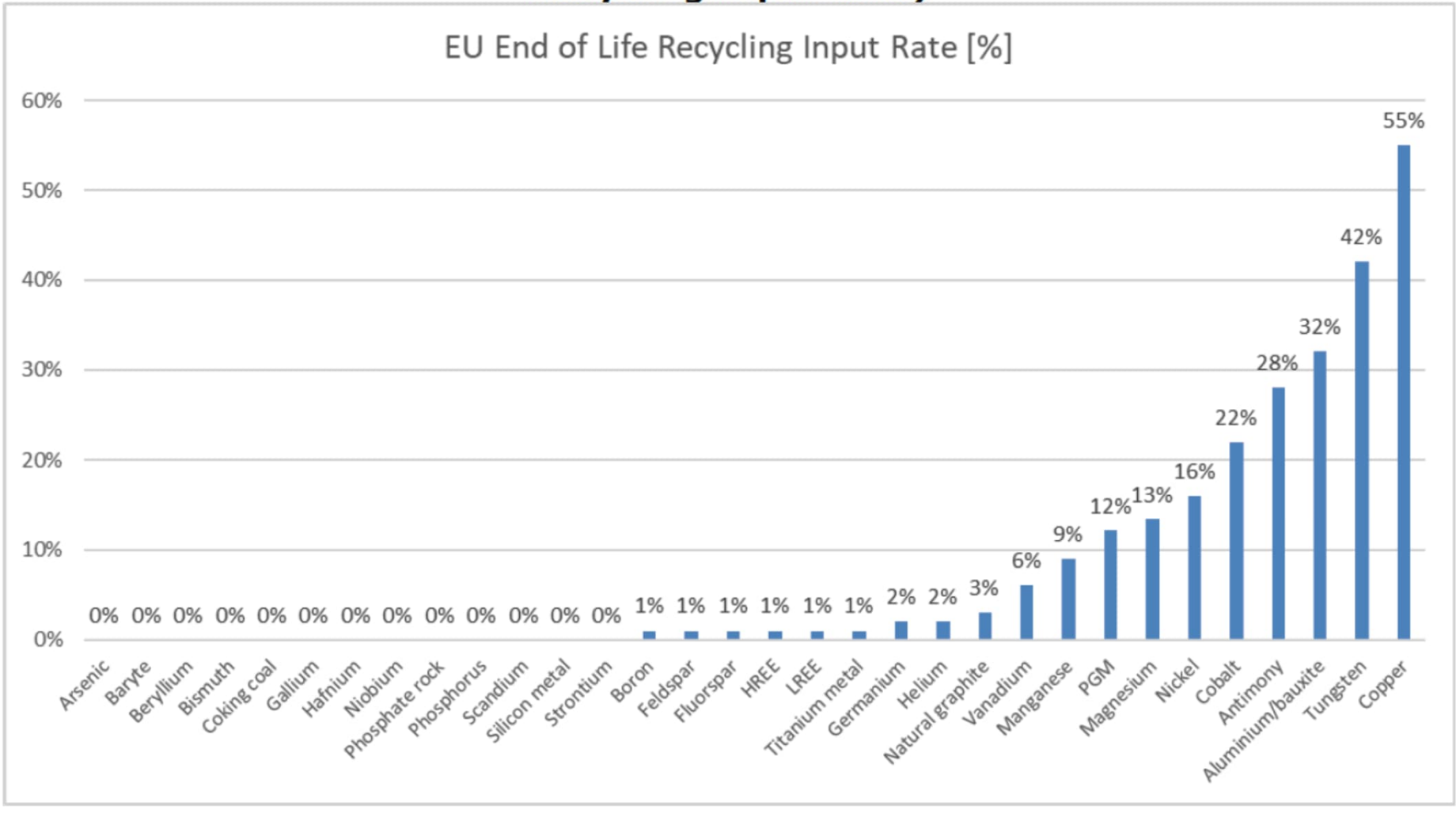


Figure D: Major EU suppliers of CRMs



Source: "European Commission, Study on the Critical Raw Materials for the EU 2023– Final Report"

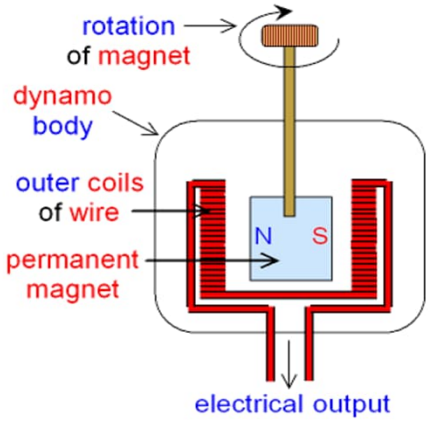
Figure F: Recycling's contribution to meeting materials demand (End of Life Recycling Input Rate)[8]



MATERIALS for ENERGY

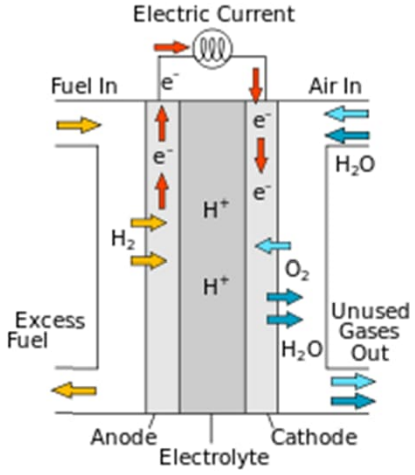
TURBINES: production of electricity from hydro, tidal, nuclear & fossil fuels

- *RE*s (= *Ln*) for magnets
- (Cu), Ag, Au for wires



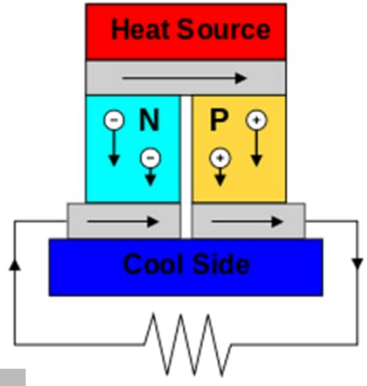
FUEL CELLS

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



PHOTOVOLTAICS

- In, Ga, etc. …

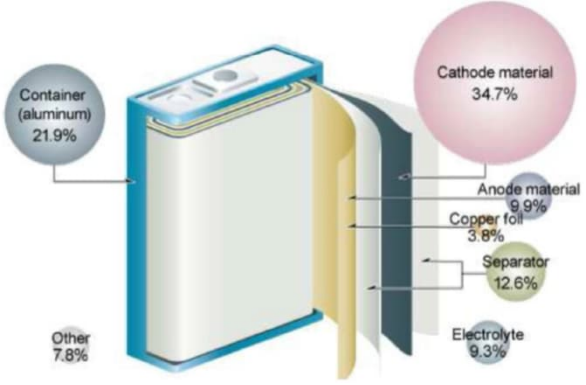


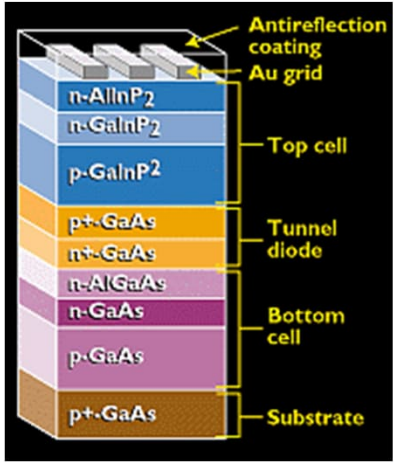
THERMOELECTRICS

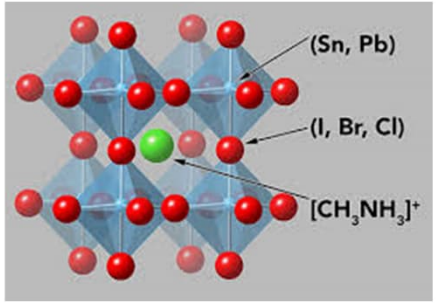
- Bi, Te, Se, Co, etc.

BATTERIES

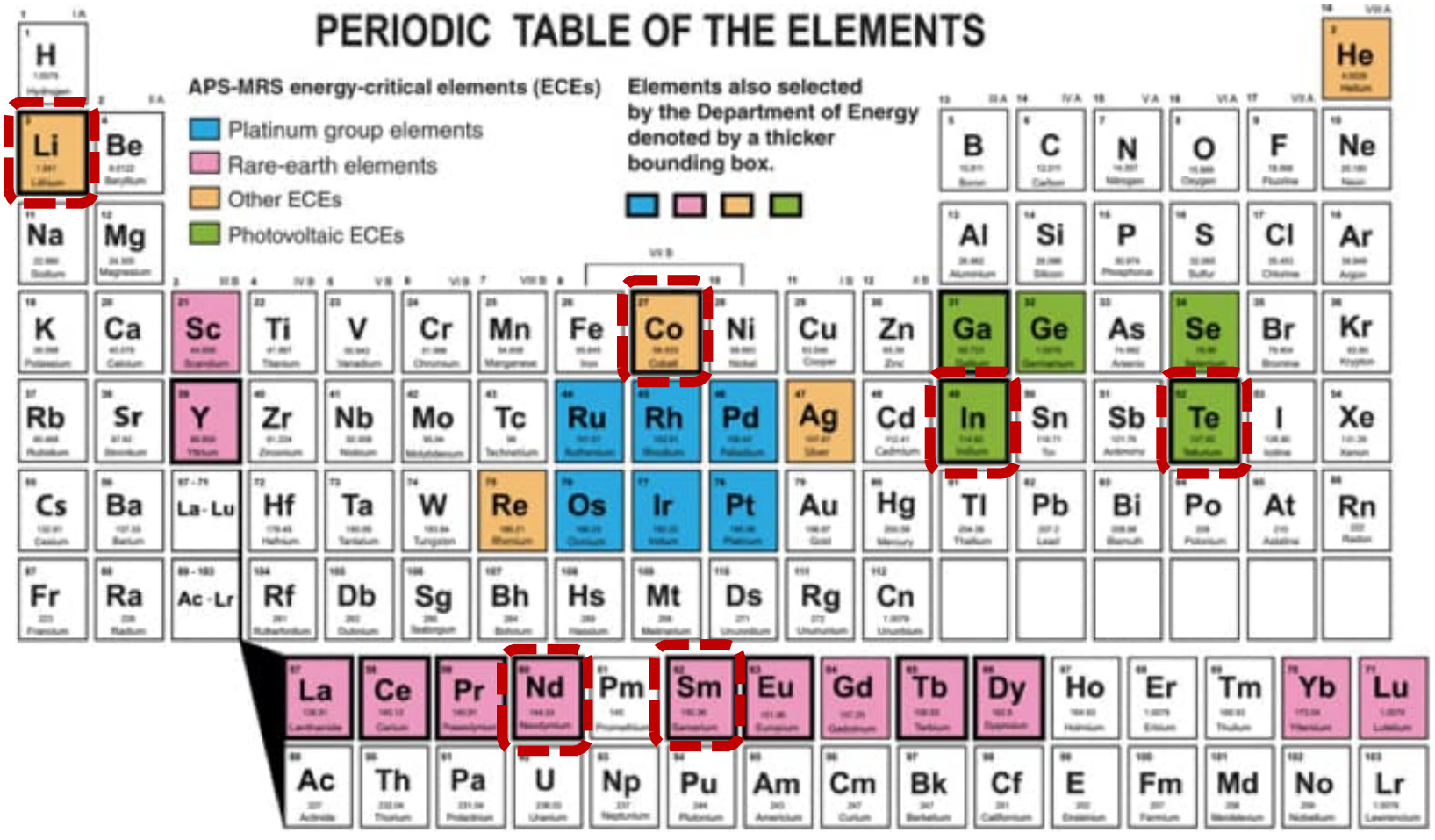
- Li, Co







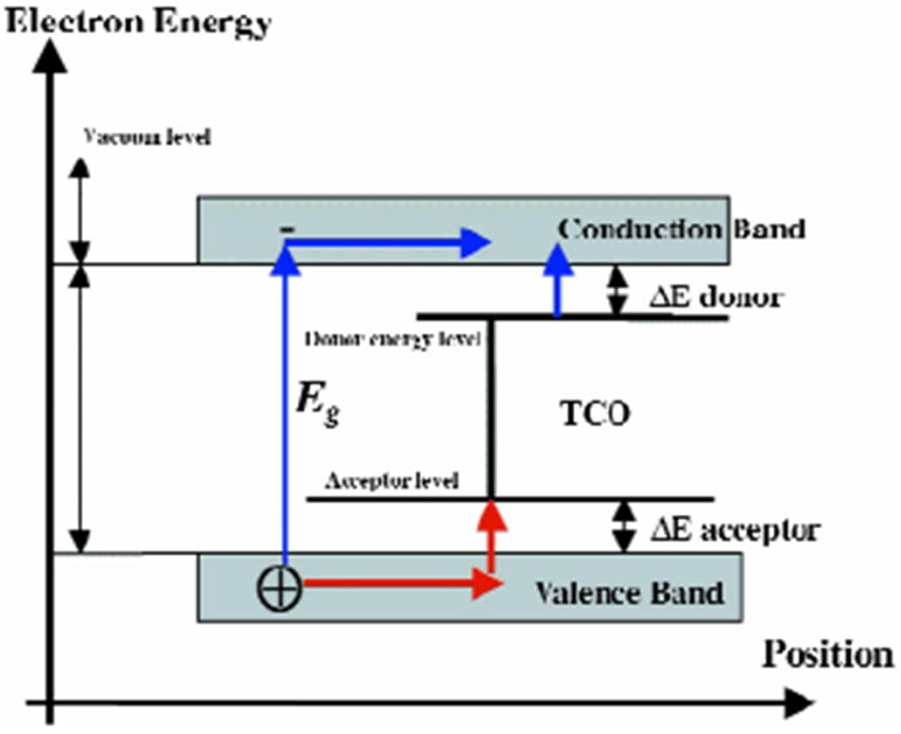
ECE: Energy Critical Elements (by APS & MRS)



WHAT SHOULD WE DO ?

- **Re-use & Re-cycle**
- **Substitute critical by non-critical**

SUBSTITUTIONS



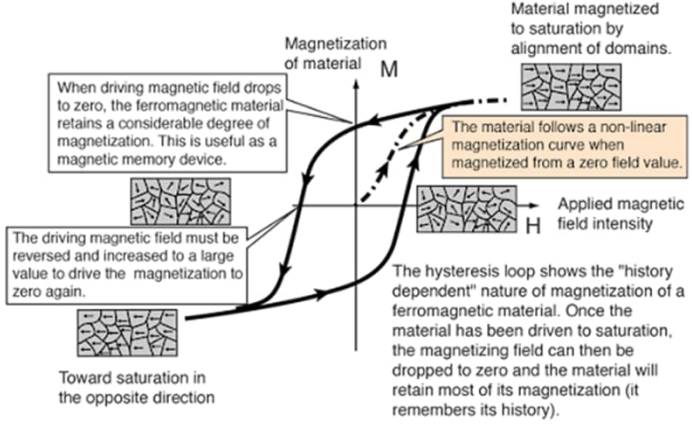
TRANSPARENT CONDUCTING OXIDES (TCOs)

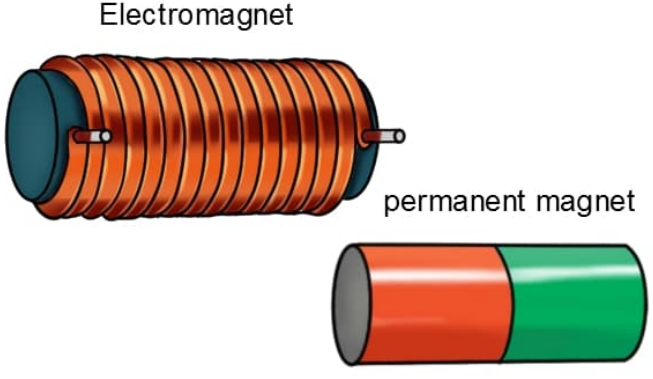
- **ITO (In-Sn-O) is the current commercial leader, but the waste recovery is very much limited**
- **F-doped SnO_2 is a good candidate**
- **Al-doped ZnO would be a highly sustainable replacement**

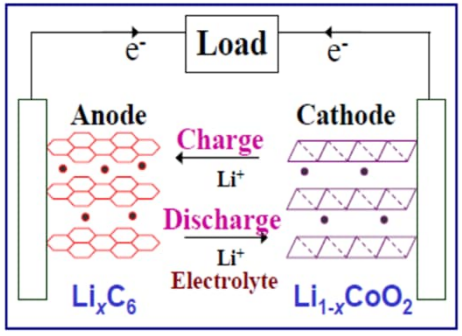
Strongest permanent magnets: $Nd_2Fe_{14}B$ & $SmCo_5$

"Non-Critical" ALTERNATIVES – Are there such ?

- **REQUIREMENTS: Curie temperature, Magnetization, Coersivity**
- **AlNiCo: "best of the rest"**
- **ε-Fe_2O_3 (difficult synthesis)**
- **Electromagnets**







EC: ethylene carbonate

DEC: dimethyl carbonate

Li-ion battery

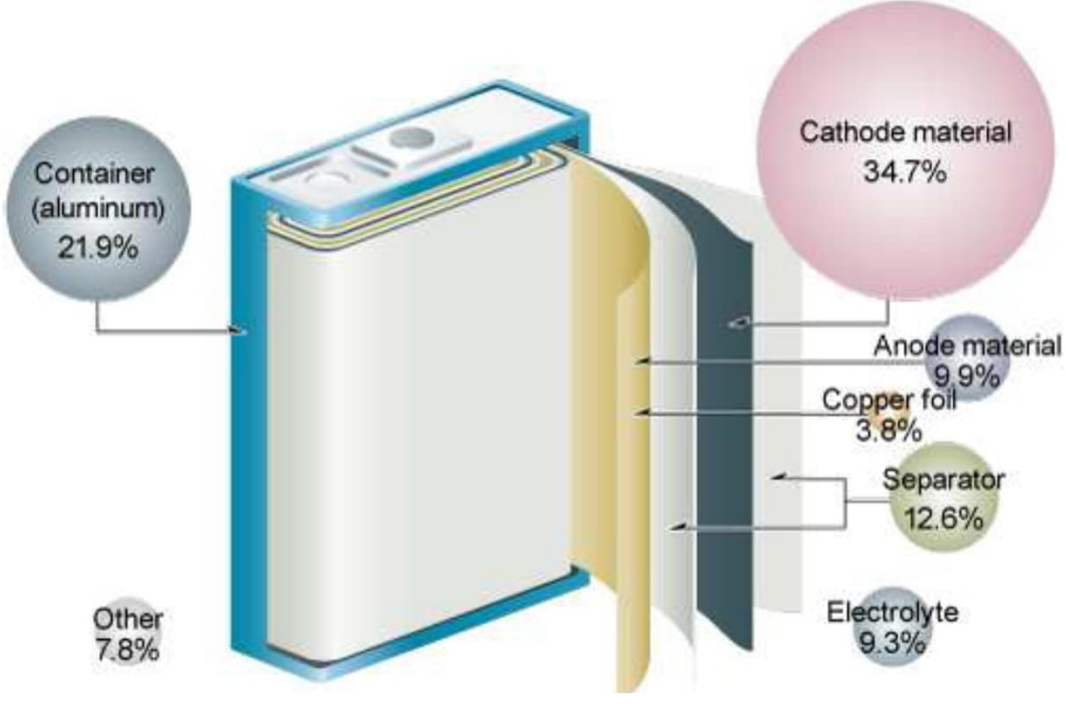
Cathode: $LiCoO_2$

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



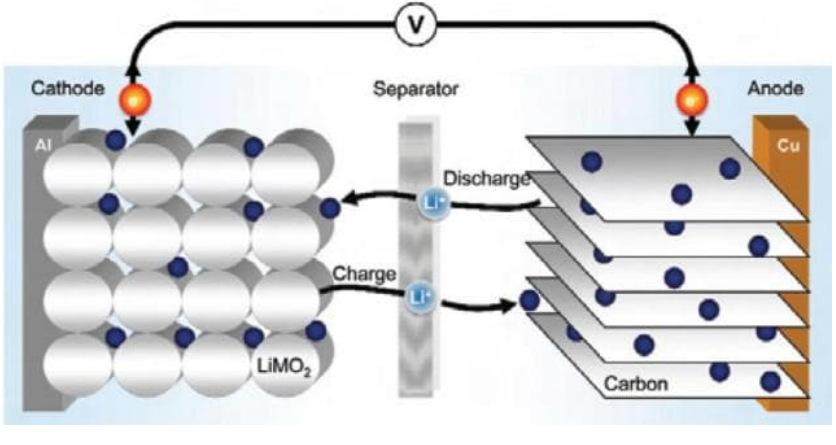
PRESENT Li-ion battery MATERIAL VARIETY

(under intense research)

CATHODE	$LiCoO_2$
	$Li(Co,Ni,Mn)O_2$ (raw mat., perfor.), $LiMn_2O_4$, $LiFePO_4$ (safety)
ANODE	Graphite
	Silicon (energy density), $Li_4Ti_5O_{12}$ (safety)
ELECTRO-LYTE	$LiPF_6$ + ethylene carbonate solution
	Solid electrolytes (safety)

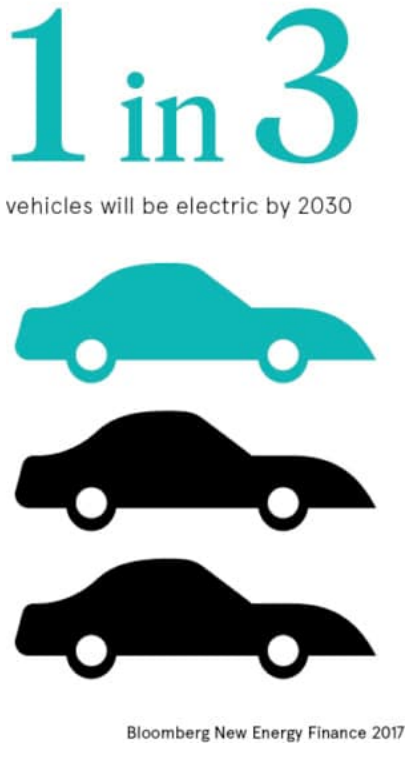
Liquid electrolyte

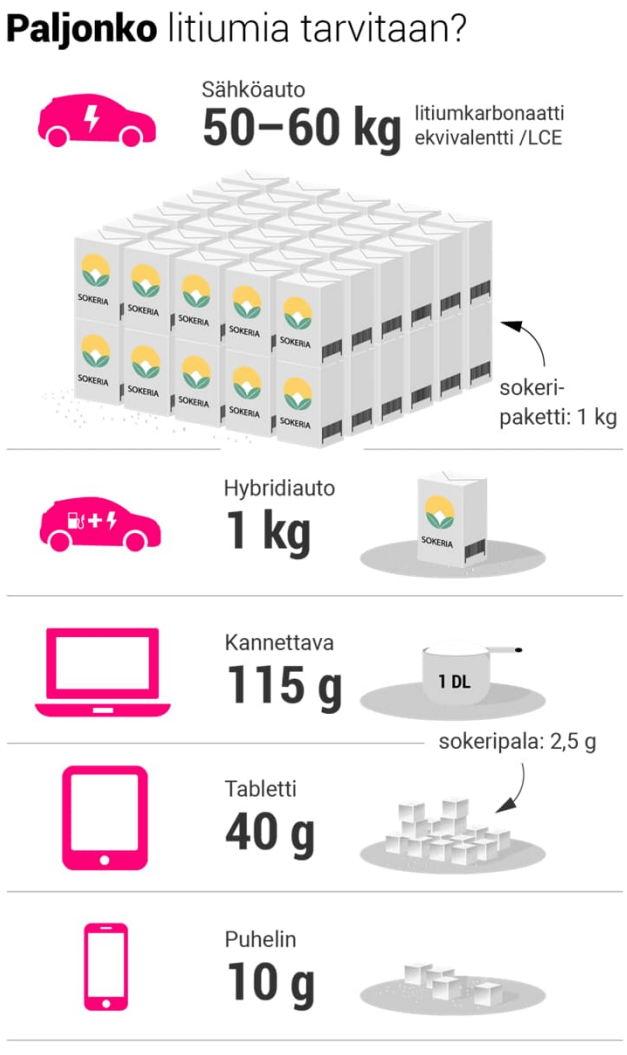
$LiCoO_2$



Graphite

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

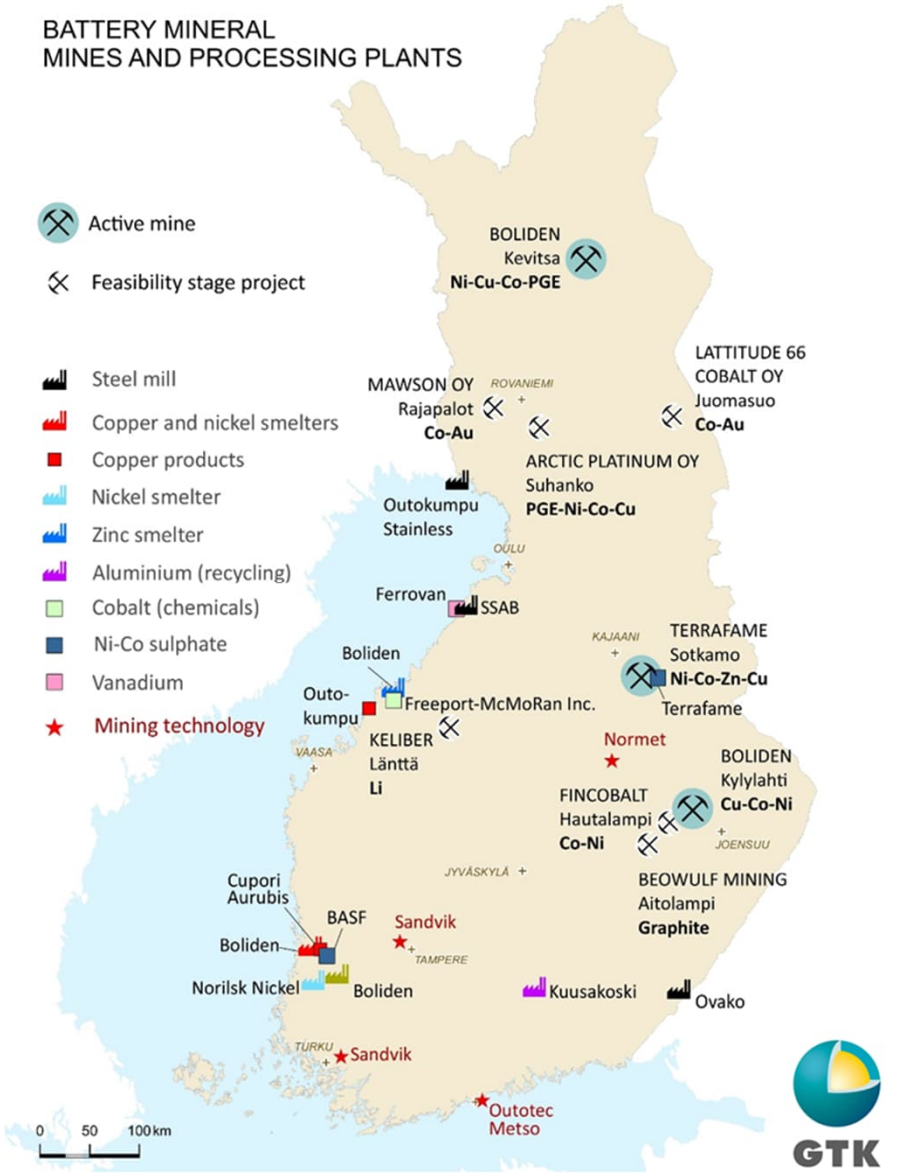
60 % of cobalt in the world is mined in Republic of Congo

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

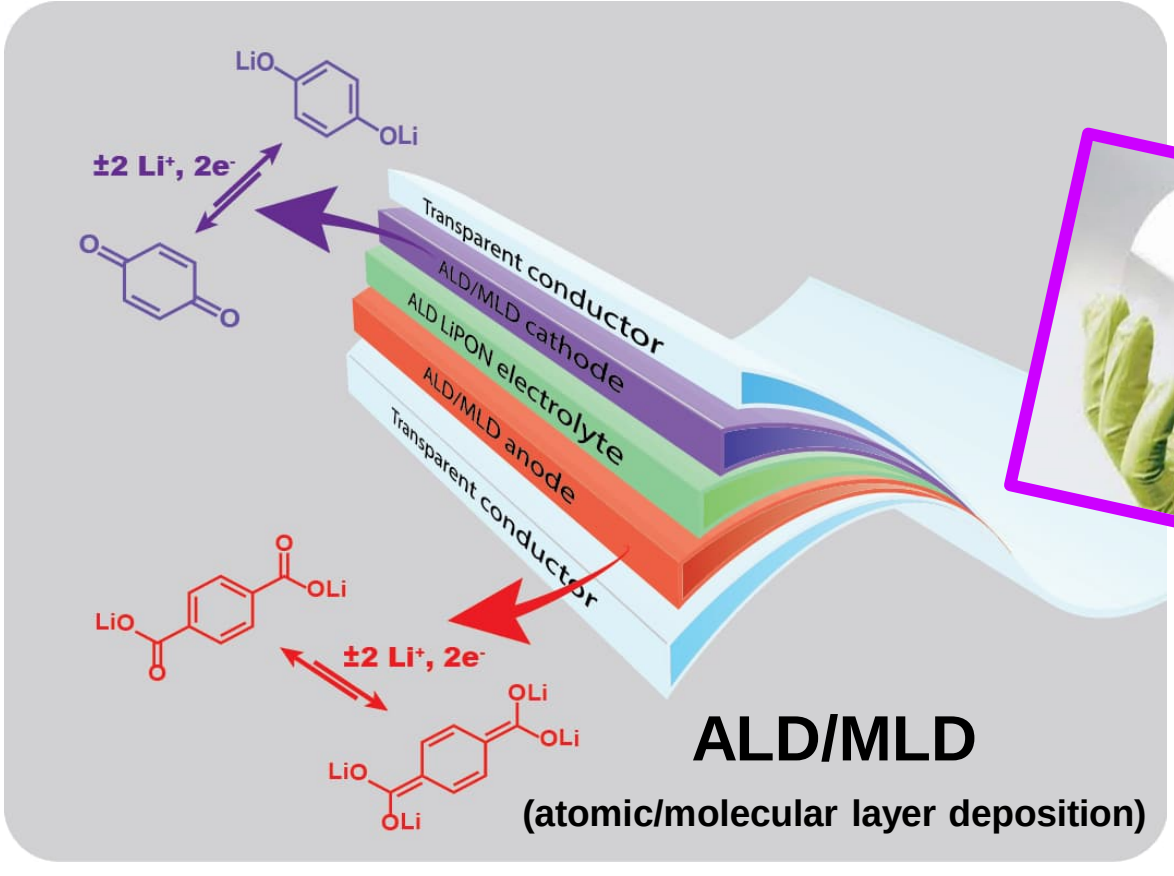
Battery Minerals in FINLAND

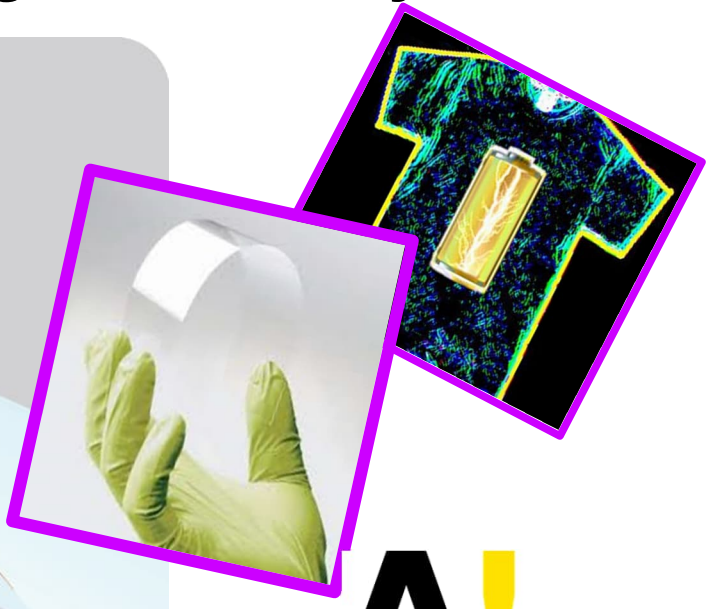
- **Mining: Ni, Cu, Co**
- **Refining: Co (13 %), Ni, Cu**
- **Planned mining/refining: Li, Co (→ 2-4 %)**

“Ethical Cobalt/Metals”



Flexible safe “metal-sparing” Li-organic battery





Aalto University
School of Engineering

TOYOTA

M. Nisula, Y. Shindo, H. Koga & M. Karppinen, ***Chem. Mater.* 27**, 6987 (2015).
M. Nisula & M. Karppinen, ***Nano Lett.* 16**, 1276 (2016).
M. Nisula & M. Karppinen, ***J. Mater. Chem. A* 6**, 7027 (2018).