

LECTURE SCHEDULE

	Date	Topic
1.	Wed 07.09.	Course Introduction & Short Review of the Elements
2.	Fri 09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon 12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri 16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon 19.09.	Transition Metals: General Aspects & Pigments
6.	Wed 21.09.	Redox Chemistry
7.	Fri 23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon 26.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
9.	Wed 28.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
10.	Fri 30.09.	Mn, Cu, Ru
11.	Mon 03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Fri 07.10.	Lanthanoids + Actinoids & Luminescence
13.	Mon 10.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
14.	Wed 12.10.	Resources of Elements & Rare/Critical Elements
15.	Fri 14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

PRESENTATION TOPICS/SCHEDULE

Fri 16.09. **Zn:** Rautakorpi, Stenbrink & Hyvärinen

Mon 26.09. **Nb:** Souza, Rahikka & Tong

Wed 28.09. **Mo:** Alimbekova & Tran (Nhi)

Ti: Mäki & Israr

Fri 30.09. **Mn:** Tao & Song (Zonghang)

Cu: Marechal, Weppe & Ishtiaq

Ru: Järvinen & Verkama

Fri 07.10. **Eu:** Bardiau, Wolfsberger & Klingerhöfer

Nd: Helminen, Olsio & Keskimaula

Mon 10.10. **U:** Airas & Holopainen

Wed 12.10. **In:** Antila & Wallius

Te: Peussa & Heylen

Fri 14.10. **Co:** Song (Yutong) & Lone

QUESTIONS: Lecture 14

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

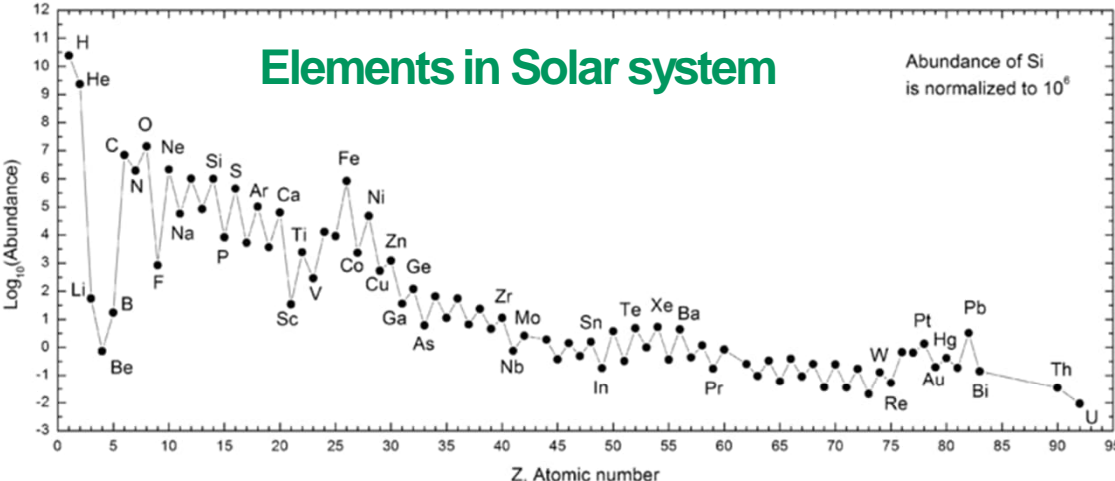
- **Absolute abundance ?**
- **Accessible resources** (distribution, technical skills, etc.) ?
- **Availability** (politics, etc.) ?

WHAT MAKES US CALL ELEMENTS CRITICAL

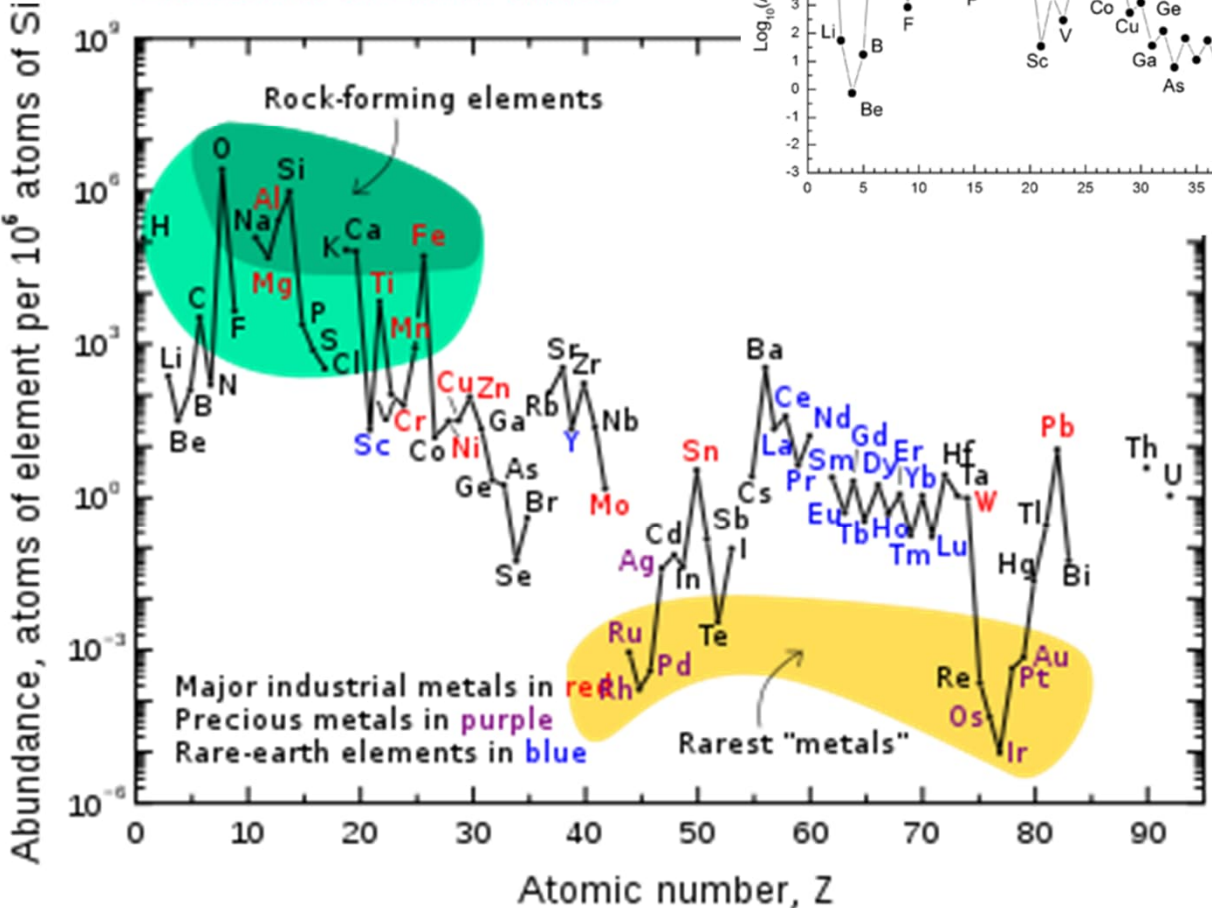
- **Essential to human health ?**
- **Needed to make crucial/desired devices ?**
- **Needed to generate/store energy ?**
- **Needed but not readily available ?**

Elements in Solar system

Abundance of Si is normalized to 10^6



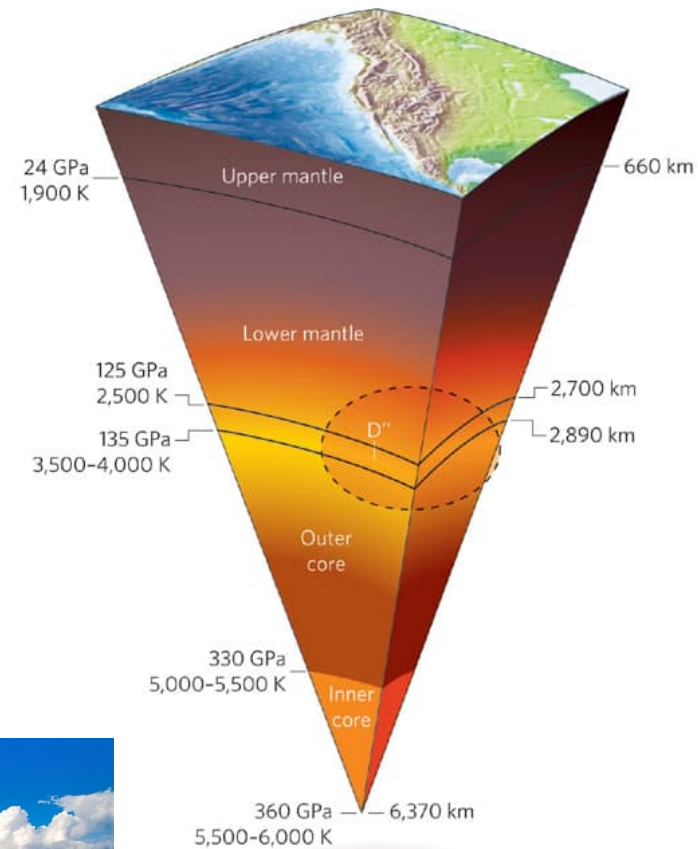
Elements in Earth crust



ABSOLUTE ABUNDANCE

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

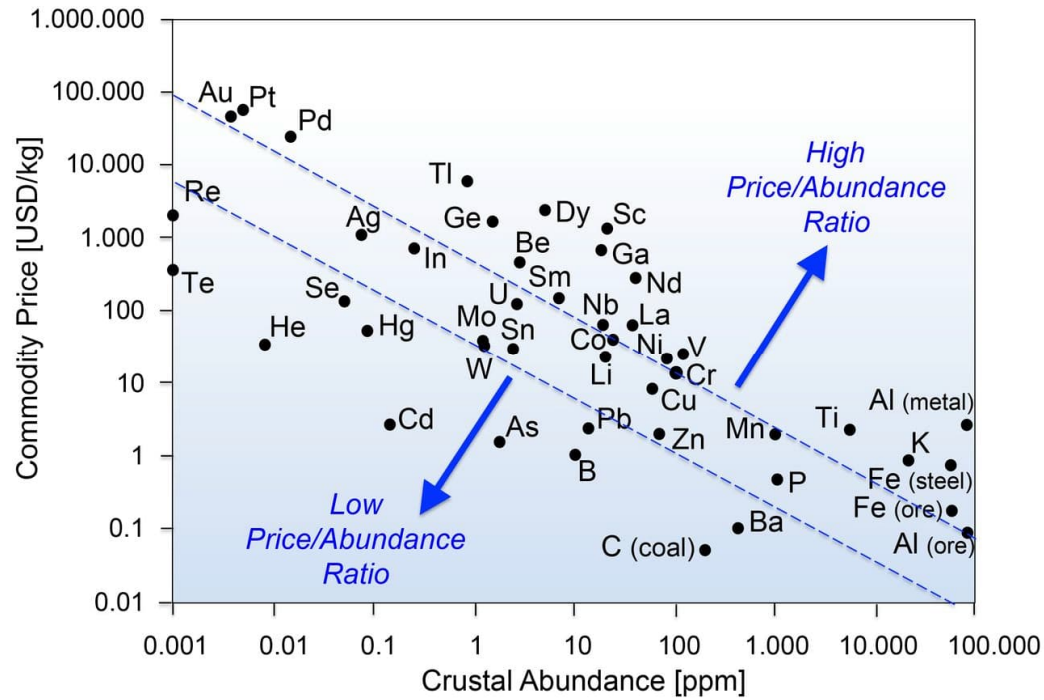


London metal exchange

	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

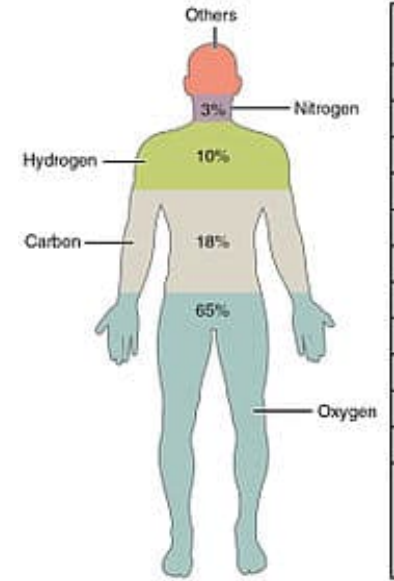
Price: affected by the rarity but also by fashion, speculation, politics, ...

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

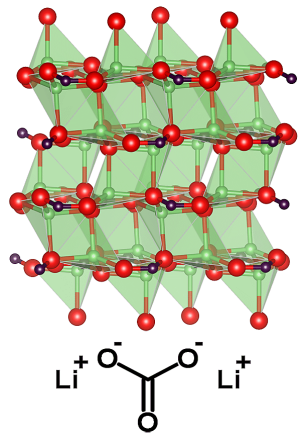


The four organic basic elements Quantity elements Essential trace elements Possible structural or functional role in mammals

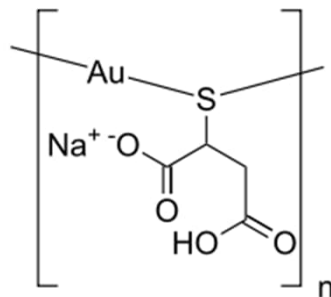


Supplement industry: \$5 billion in sales

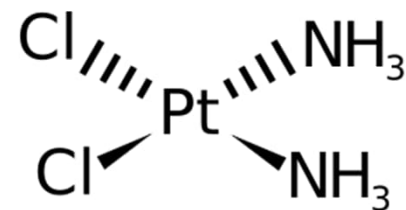
CRITICAL as MEDICINE



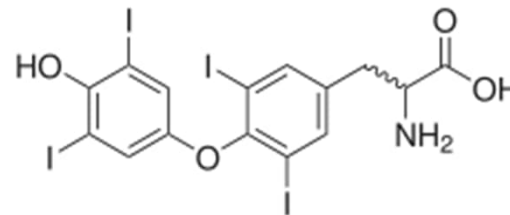
Li₂CO₃ for depression



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														

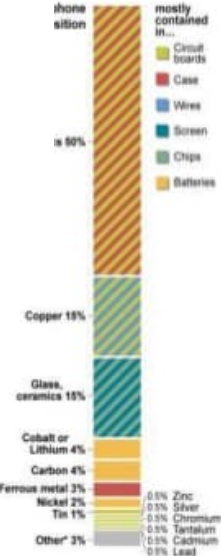
Elements used in the production of components for computers

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.



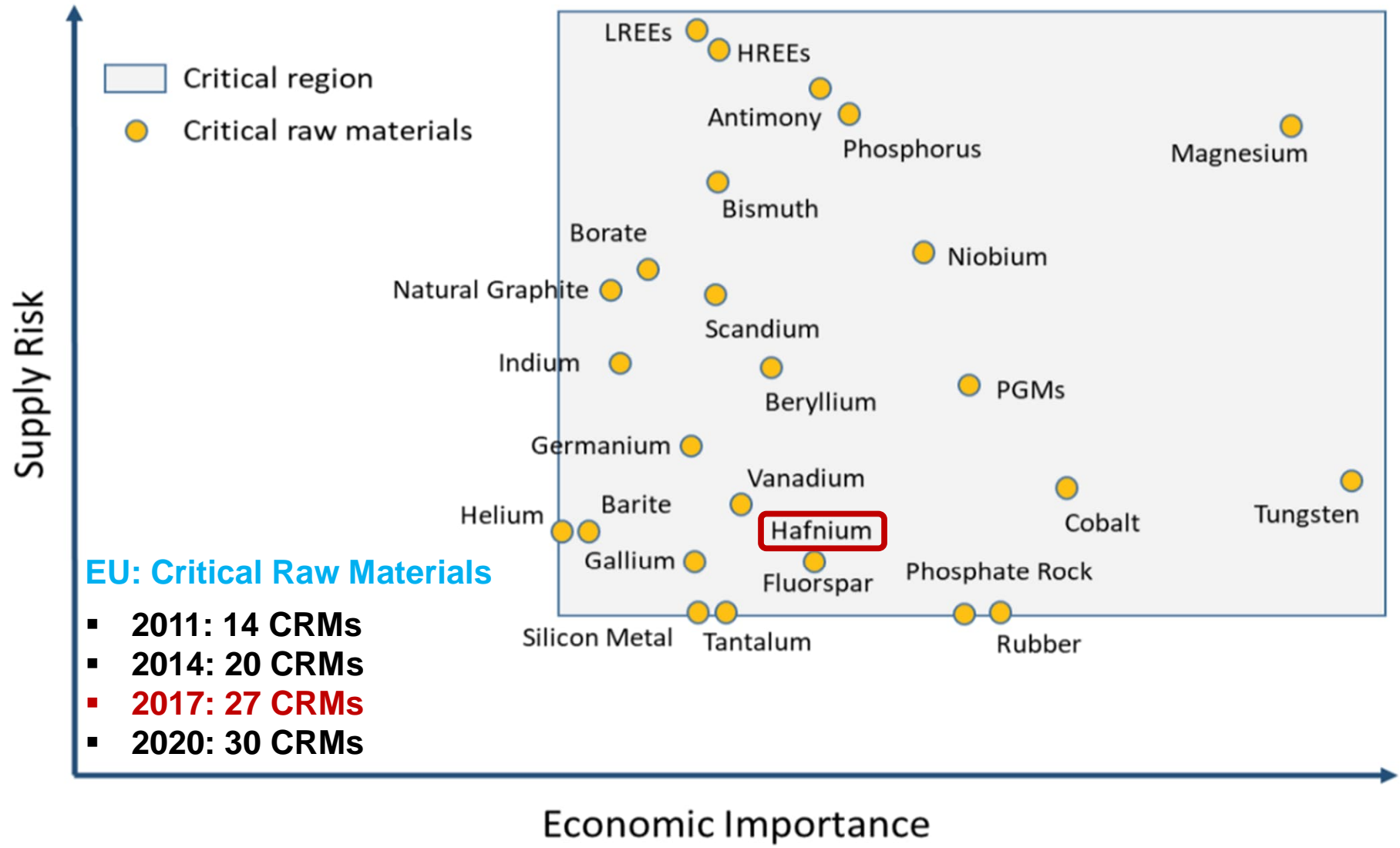
A mobile phone weighing 100 g contains:

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



Courtesy of Dr Mike Pitts
Sustainability Manager

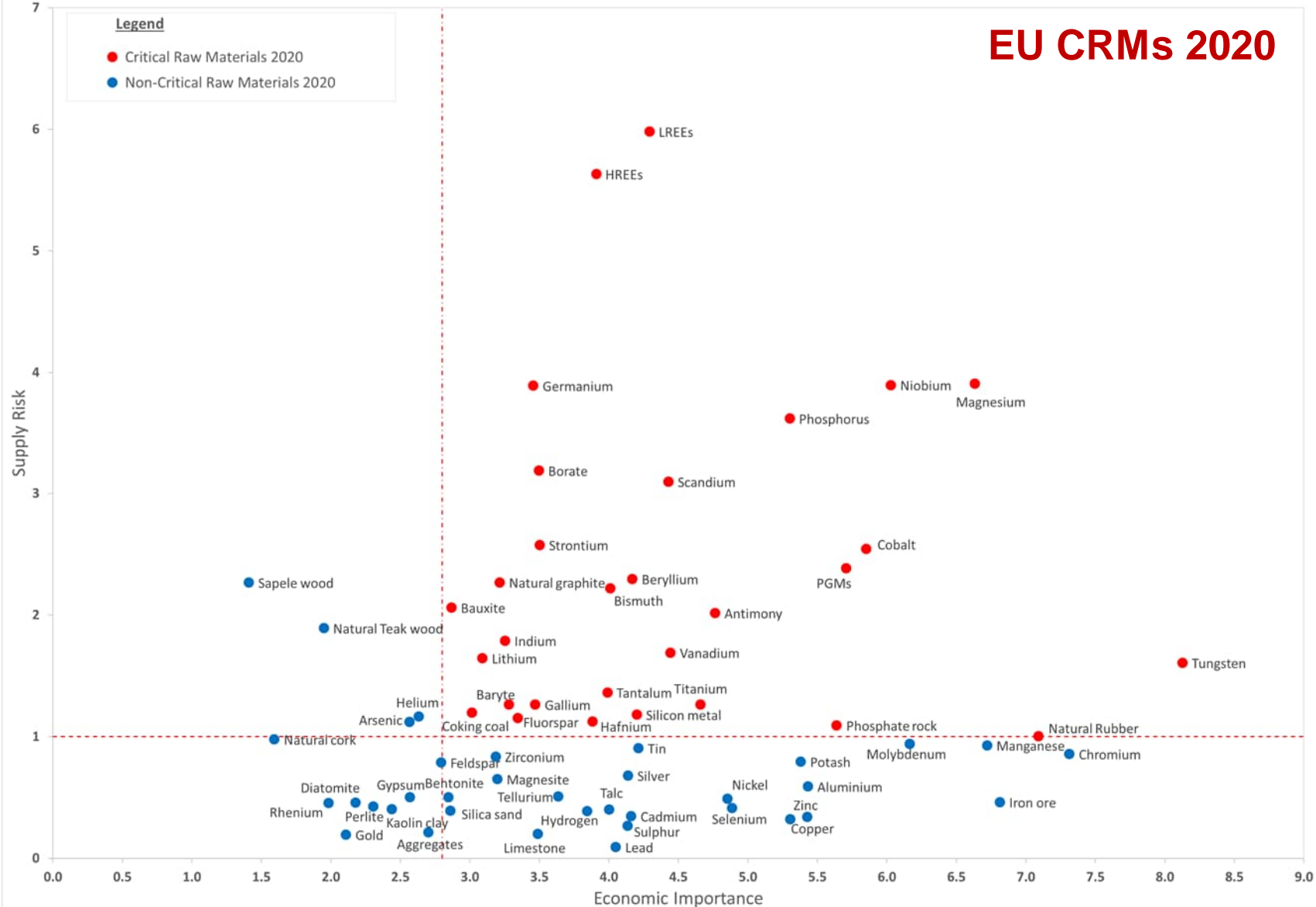
Source: Basel Convention, 2006; Lindholm (Nokia report), 2003



EU: Critical Raw Materials

- **2011: 14 CRMs**
- **2014: 20 CRMs**
- **2017: 27 CRMs**
- **2020: 30 CRMs**

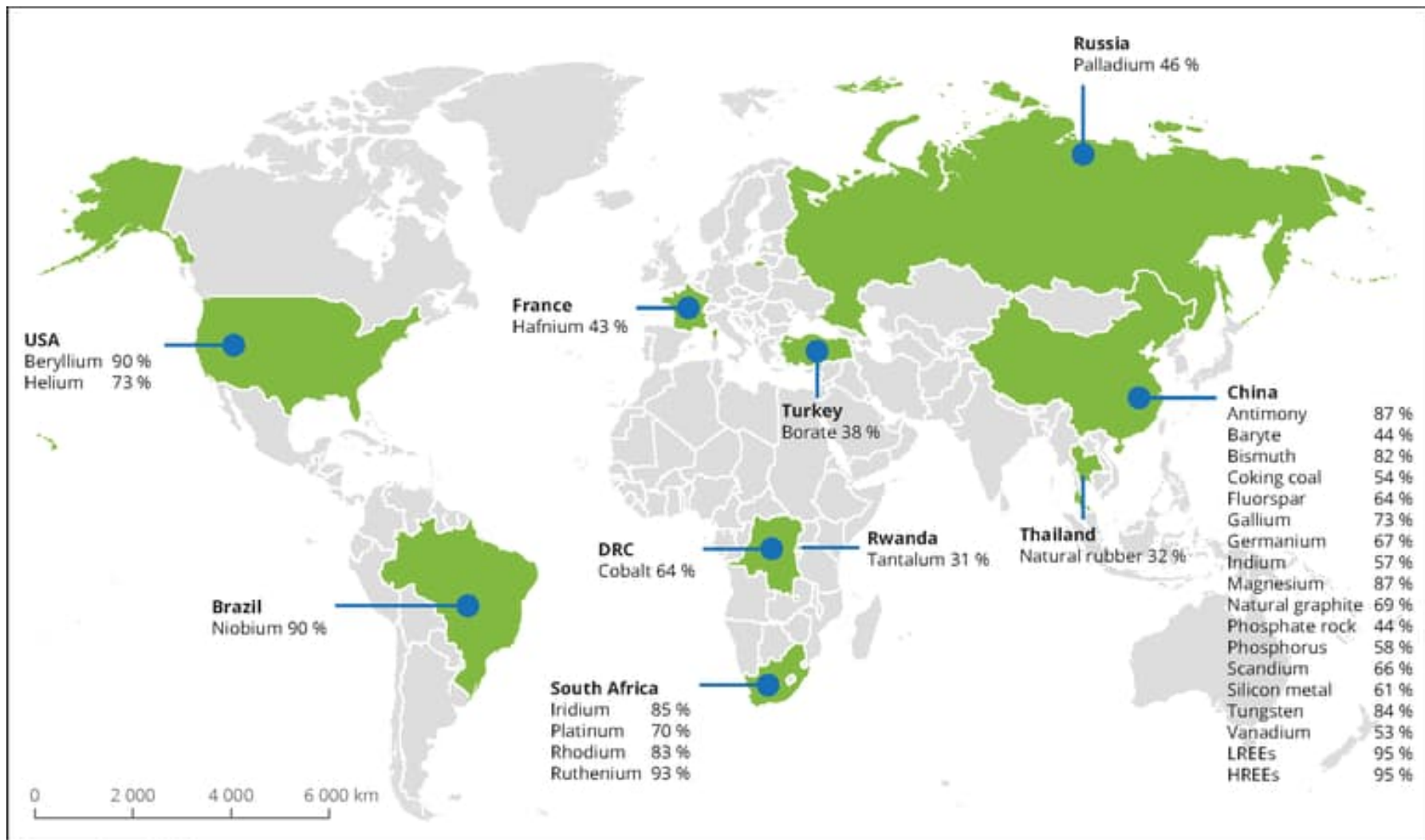
EU CRMs 2020



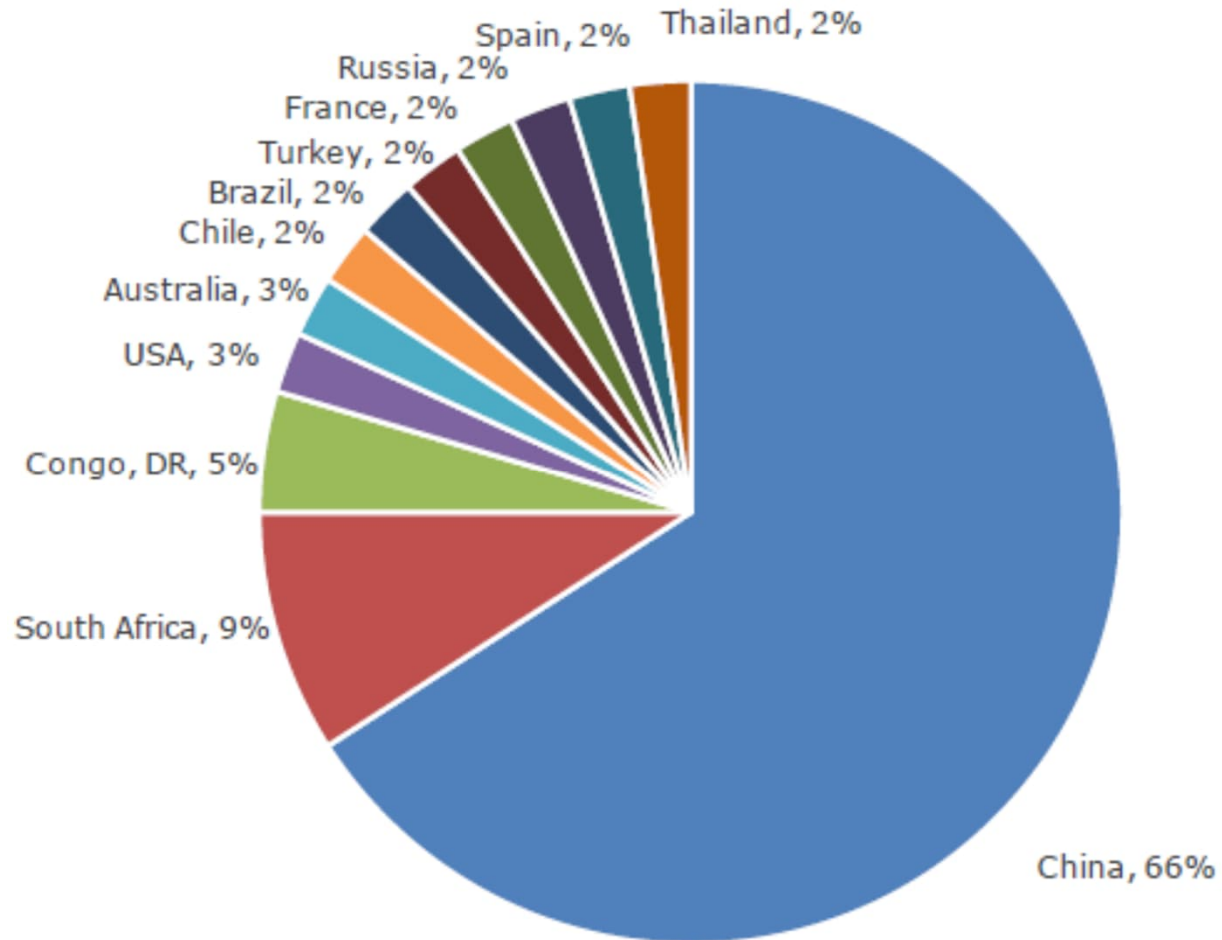
2020 Critical Raw Materials (new as compared to 2017 in bold)

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 ?



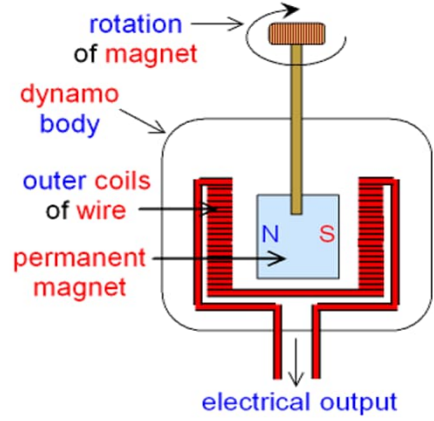
FROM WHICH COUNTRIES THE CRITICAL ELEMENTS/RAW MATERIALS COME TO EU CURRENTLY ?



MATERIALS for ENERGY

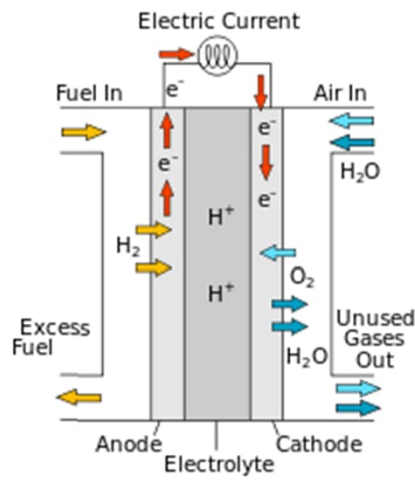
TURBINES: production of electricity from hydro, tidal, nuclear & fossil fuels

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



FUEL CELLS

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

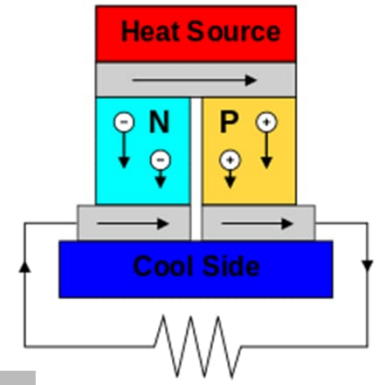


PHOTOVOLTAICS

- In, Ga, etc. ...

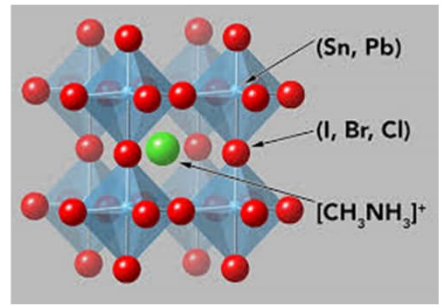
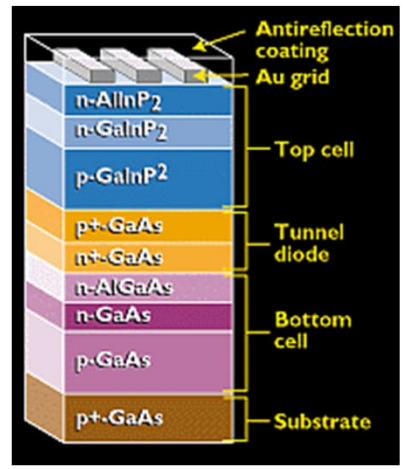
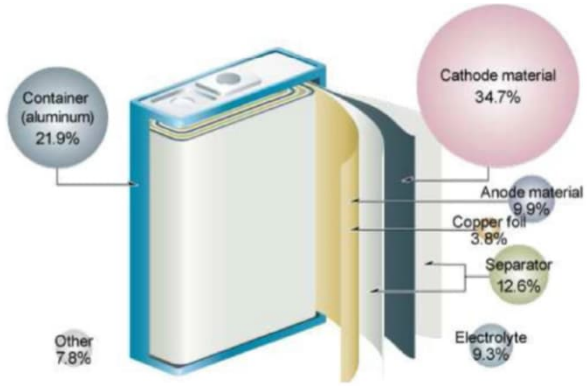
THERMOELECTRICS

- Bi, Te, Se, Co, etc.



BATTERIES

- Li, Co



WHAT SHOULD WE DO ?

➤ Re-use & Re-cycle

➤ **Substitute critical by non-critical**



CONTRIBUTION of RECYCLING: TOO SMALL !

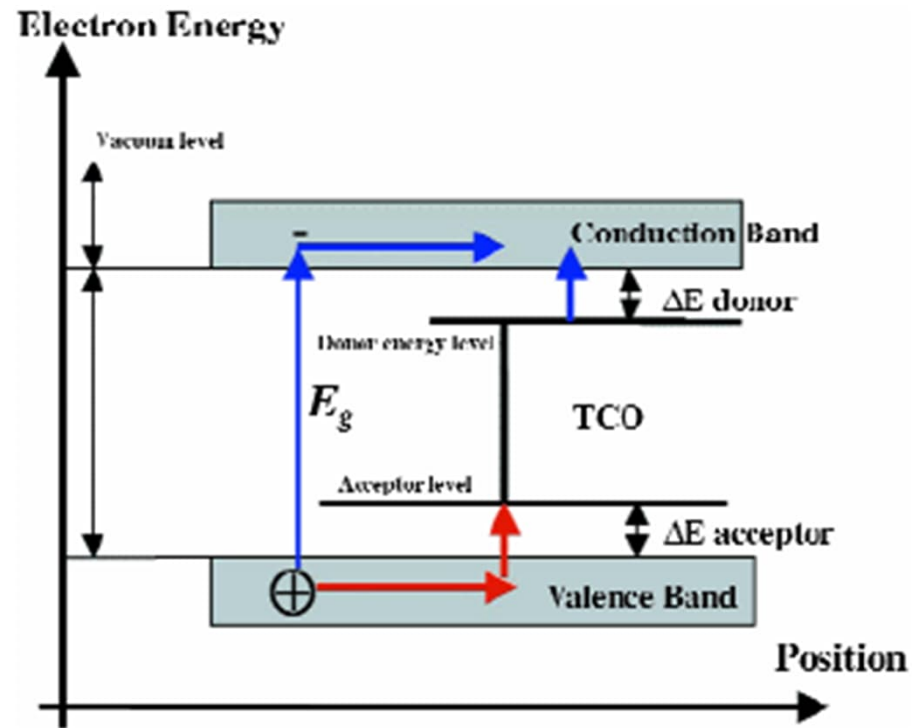
End-of-life recycling input rate (EOL-RIR) [%]

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	La-Lu ¹	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
Fr	Ra	Ac-Lr ²	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo			



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

SUBSTITUTIONS



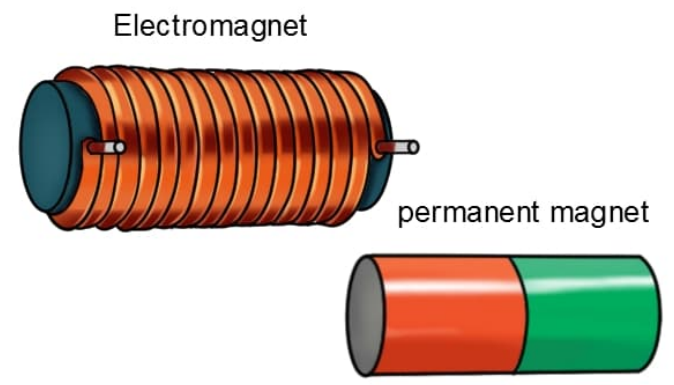
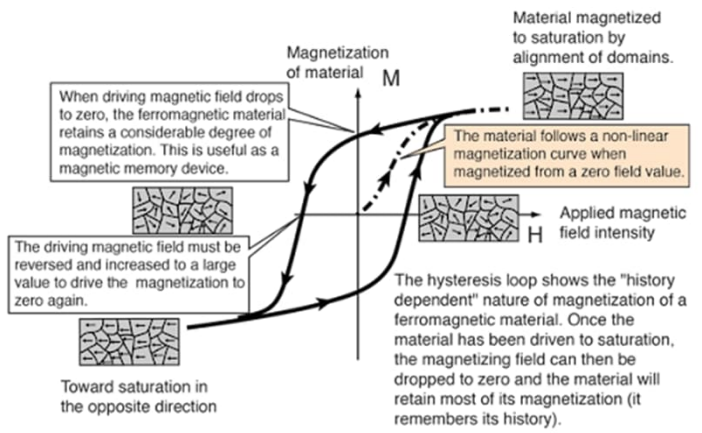
TRANSPARENT CONDUCTING OXIDES (TCOs)

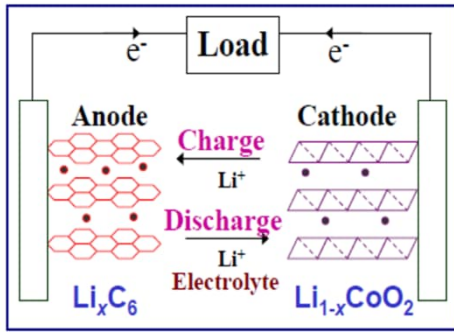
- ITO (**In**-Sn-O) is the current commercial leader, but the waste recovery is very much limited
- F-doped SnO_2 is a good candidate
- Al-doped ZnO would be a highly sustainable replacement

Strongest permanent magnets: $\text{Nd}_2\text{Fe}_{14}\text{B}$ & SmCo_5

“Non-Critical” ALTERNATIVES – Are there such ?

- REQUIREMENTS: Curie temperature, Magnetization, Coersivity
- AlNiCo: “best of the rest”
- $\epsilon\text{-Fe}_2\text{O}_3$ (difficult synthesis)
- Electromagnets





EC: ethylene carbonate

DEC: dimethyl carbonate

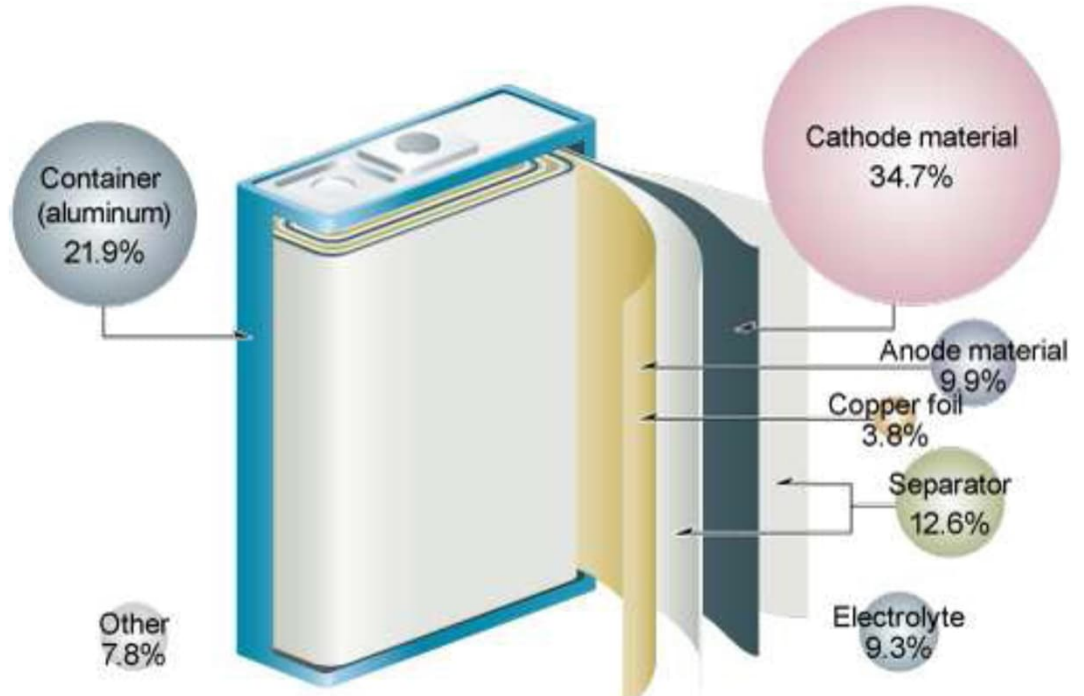
Cell: (-) C | LiPF₆-(EC+DEC) | LiCoO₂ (+)

Cathode: $\text{LiCoO}_2 \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$

Anode: $6\text{C} + x\text{Li}^+ + xe^- \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_x\text{C}_6$

Total: $\text{LiCoO}_2 + 6\text{C} \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6$

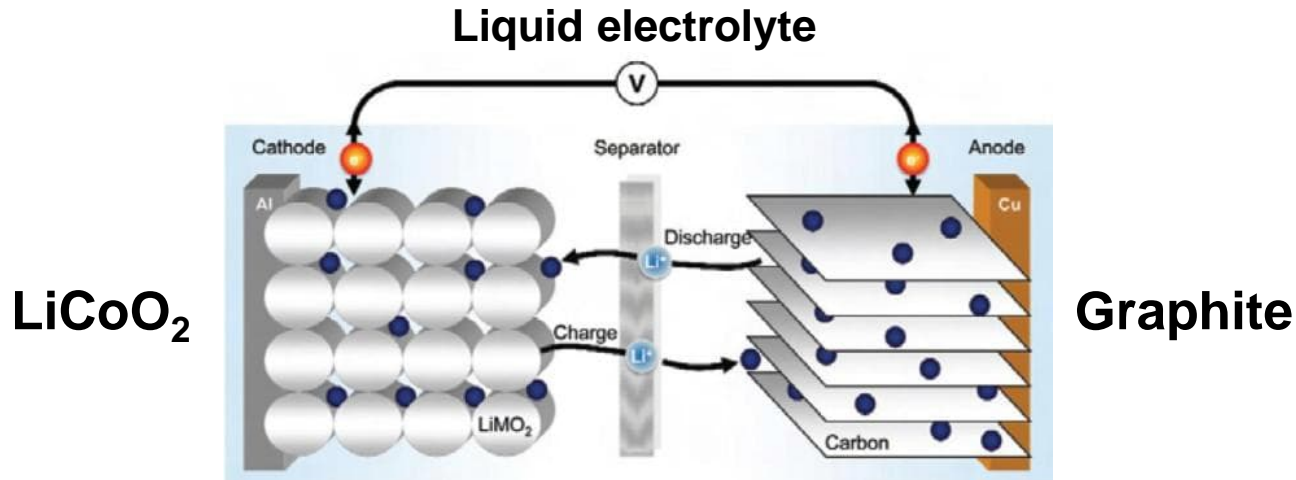
Li-ion battery
Cathode: LiCoO₂



PRESENT Li-ion battery MATERIAL VARIETY

(under intense research)

CATHODE	LiCoO₂ Li(Co,Ni,Mn)O₂ (raw mat., perfor.), LiMn₂O₄ , LiFePO₄ (safety)
ANODE	Graphite Silicon (energy density), Li₄Ti₅O₁₂ (safety)
ELECTRO- LYTE	LiPF₆ + ethylene carbonate solution Solid electrolytes (safety)



In 2030 one third of cars will be electric !

1 in 3

vehicles will be electric by 2030



Bloomberg New Energy Finance 2017

Paljonko litiumia tarvitaan?



Sähköauto

50–60 kg

litiumkarbonaatti
ekvivalentti /LCE



sokeri-
paketti: 1 kg



Hybridiauto

1 kg



Kannettava

115 g



sokeripala: 2,5 g



Tabletti

40 g



Puhelin

10 g



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**

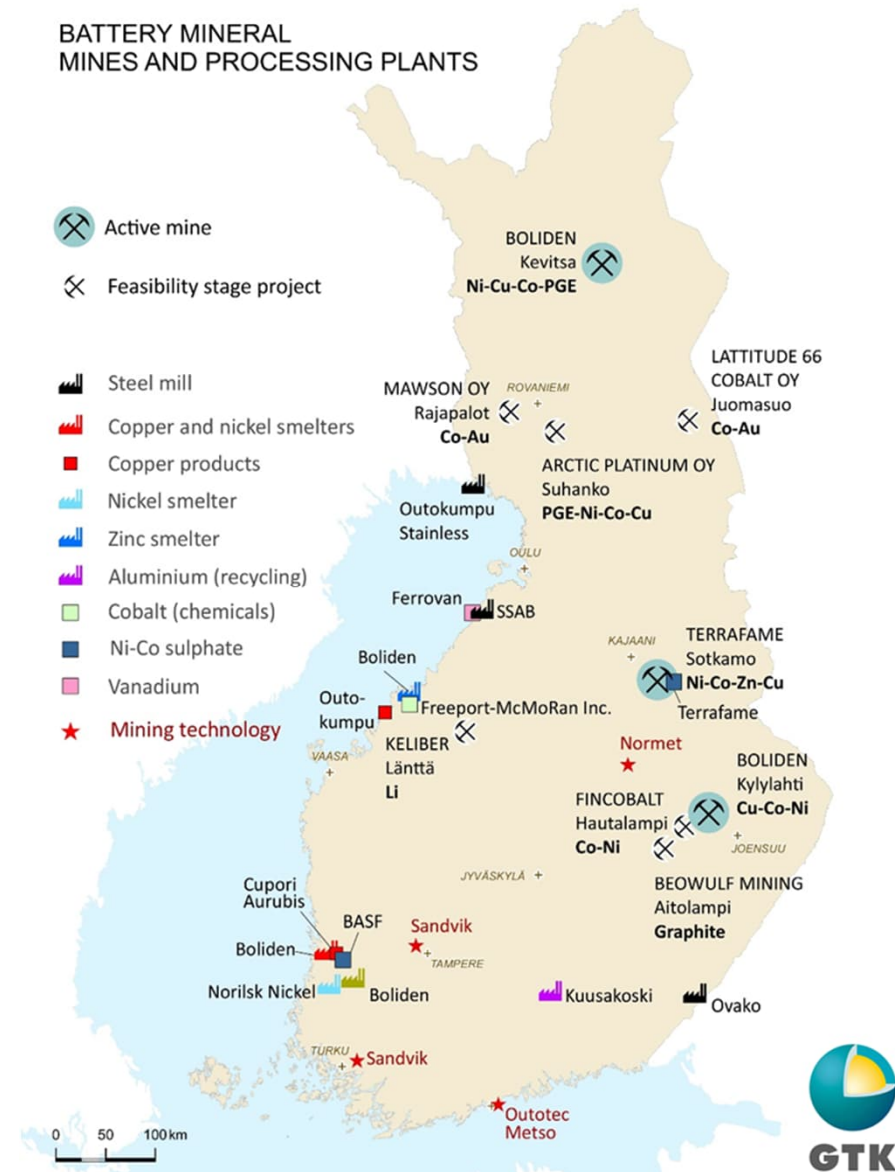


Cobalt mining place in Congo close
to Kasulo. Valokuvat: Siddharth Kara

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
Inorganic 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
LiCoO₂ cathode materials,
Journal of Power Sources **450**, 227630 (2020).

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**



OUTOTEC OYJ PRESS RELEASE NOVEMBER 1, 2018 AT 1:00 PM

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.

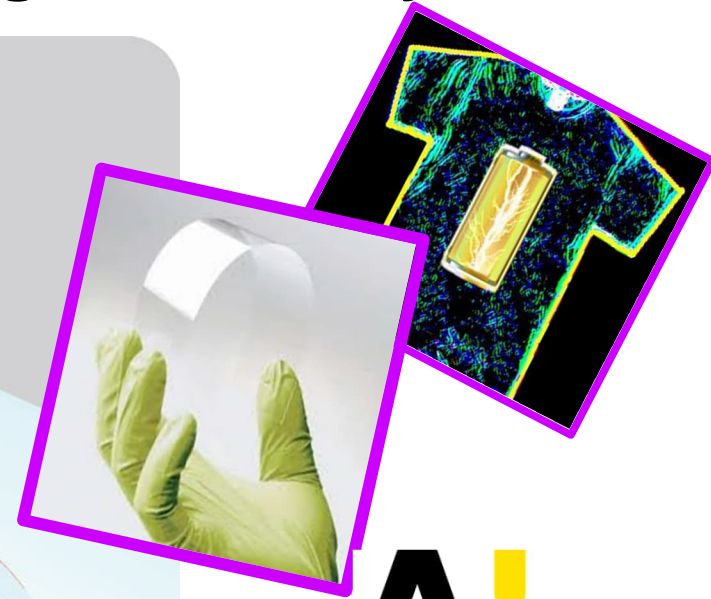
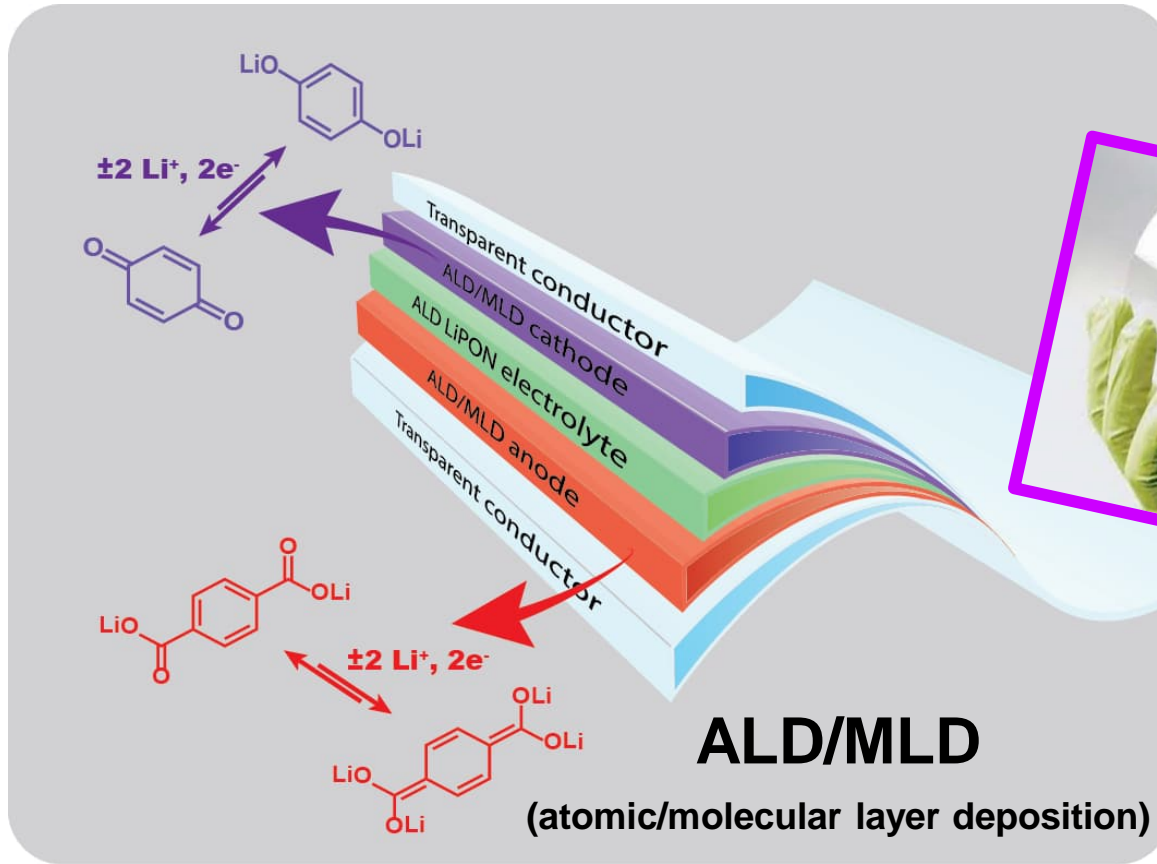
Due to the rapidly growing demand for electric cars, the recycling of battery raw materials and equipment will become ever more important. The European Commission has compiled a

0 likes 0 comments

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



A!
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).