

# LECTURE SCHEDULE

	Date	Topic
1.	Wed 28.10.	Course Introduction & Short Review of the Elements
2.	Fri 30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri 06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed 11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri 13.11.	Redox Chemistry
6.	Mon 16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed 18.11.	Zn, Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri 20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon 23.11.	Cr, Mo, W & 2D materials
10	Wed 25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri 27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon 30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed 02.12.	Inorganic Materials Chemistry Research

**EXAM:** Thu Dec 10, 9:00-12:00 (IN ZOOM)

## PRESENTATION TOPICS/SCHEDULE

- Wed 18.11.      Ti: Ahonen & Ivanoff
- Mon 23.11.      Mo: Kittilä & Kattelus
- Wed 25.11.      Mn: Wang & Tran  
Ru: Mäki & Juopperi
- Fri 27.11.      In: Suortti & Räsänen  
Te: Kuusivaara & Nasim
- Mon 30.11.      Eu: Morina  
U: Musikka & Seppänen

## **QUESTIONS: Lecture 11**

- **Give three examples of seriously critical elements**
- **Discuss shortly three chemistry approaches to solve the problems related to the CRMs**

## WHAT MAKES US CALL ELEMENTS RARE ?

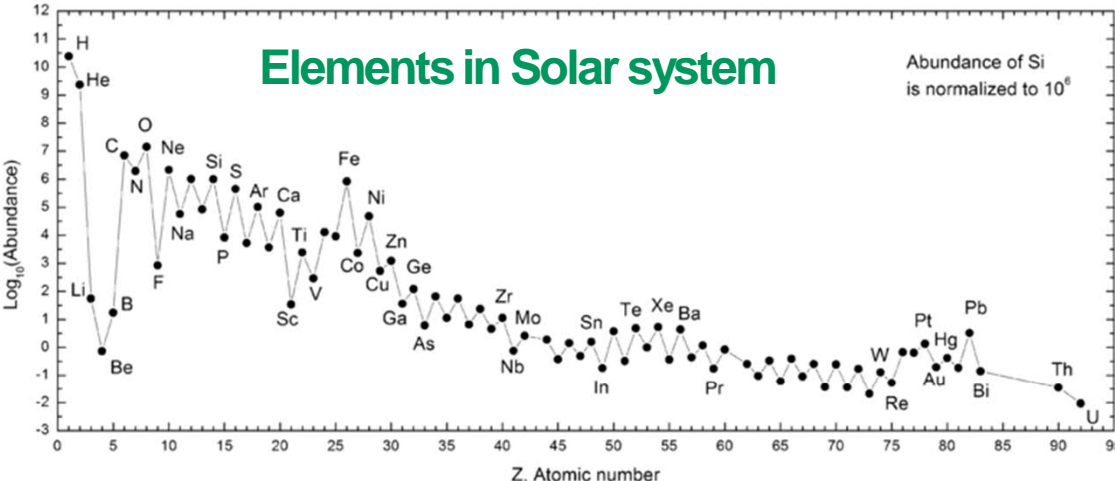
- **Absolute abundance**
- **Accessible resources** (distribution, technical skills, etc.)
- **Availability** (politics, etc.)

## WHAT MAKES US CALL ELEMENTS CRITICAL ?

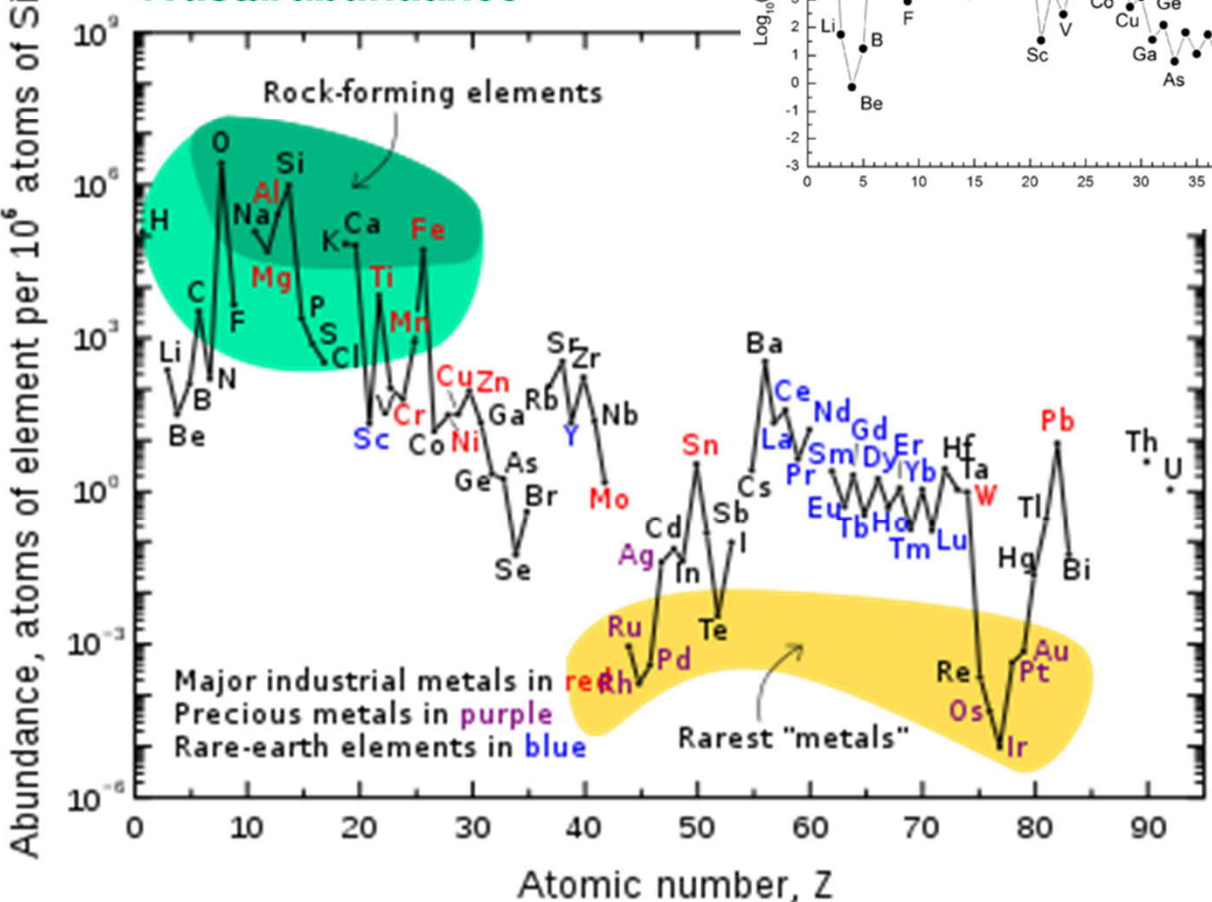
- **Essential to human health**
- **Needed to make crucial/desired devices**
- **Needed to generate/store energy**
- **Needed but not readily available**

# Elements in Solar system

Abundance of Si is normalized to  $10^6$



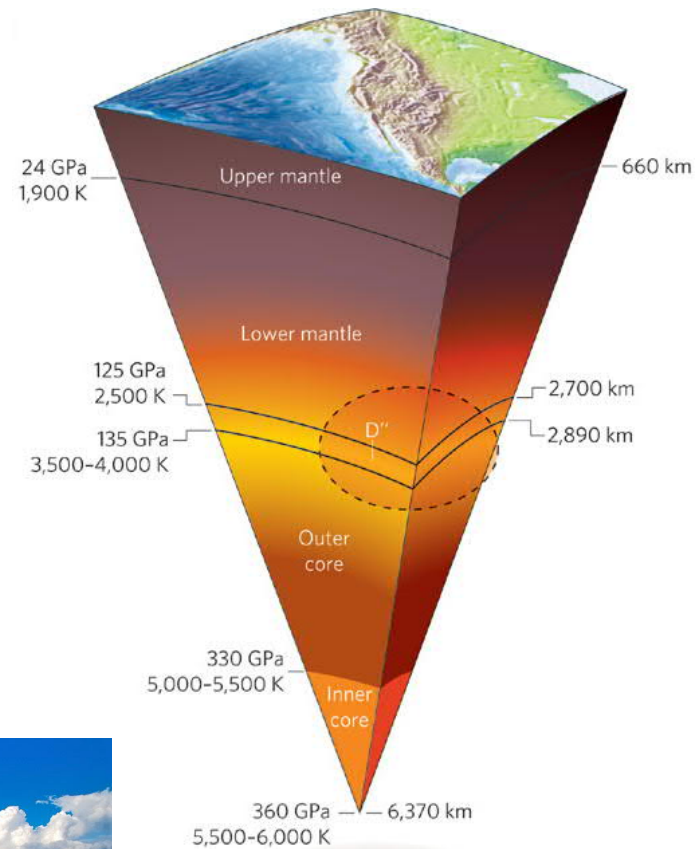
# Crustal abundance



# ABSOLUTE ABUNDANCE

# ACCESSIBLE RESOURCES

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



# Remaining Known Usable Reserves of the Elements

1 <b>H</b> 1.00794																	2 <b>He</b> 4.002602
3 <b>Li</b> 6.941	4 <b>Be</b> 9.012182											5 <b>B</b> 10.811	6 <b>C</b> 12.0107	7 <b>N</b> 14.00674	8 <b>O</b> 15.9994	9 <b>F</b> 18.99840	10 <b>Ne</b> 20.1797
11 <b>Na</b> 22.98977	12 <b>Mg</b> 24.3050											13 <b>Al</b> 26.98153	14 <b>Si</b> 28.0855	15 <b>P</b> 30.97376	16 <b>S</b> 32.066	17 <b>Cl</b> 35.4527	18 <b>Ar</b> 39.948
19 <b>K</b> 39.0983	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.95591	22 <b>Ti</b> 47.867	23 <b>V</b> 50.9415	24 <b>Cr</b> 51.9961	25 <b>Mn</b> 54.93804	26 <b>Fe</b> 55.845	27 <b>Co</b> 58.93320	28 <b>Ni</b> 58.6934	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92160	34 <b>Se</b> 78.96	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80
37 <b>Rb</b> 85.4678	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.9085	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.90638	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.9055	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.8682	48 <b>Cd</b> 112.411	49 <b>In</b> 114.818	50 <b>Sn</b> 118.760	51 <b>Sb</b> 121.760	52 <b>Te</b> 127.60	53 <b>I</b> 126.9044	54 <b>Xe</b> 131.29
55 <b>Cs</b> 132.9054	56 <b>Ba</b> 137.327	57 <b>La *</b> 138.9055	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.9479	74 <b>W</b> 183.84	75 <b>Re</b> 186.207	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.217	78 <b>Pt</b> 195.078	79 <b>Au</b> 196.9665	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.3833	82 <b>Pb</b> 270.2	83 <b>Bi</b> 208.9804	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)
87 <b>Fr</b> (223)	88 <b>Ra</b> 226.025	89 <b>Ac ‡</b> (227)	104 <b>Rf</b> (257)	105 <b>Db</b> (260)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>Ds</b> (271)	111 <b>Rq</b> (272)	112 <b>Uub</b> (285)	113 <b>Uut</b> (284)	114 <b>Uuq</b> (289)	115 <b>Uup</b> (288)	116 <b>Lv</b> (292)	117 <b>Uus</b> (292)	118 <b>Uuo</b> (292)

Remaining years of availability based on the current rate of use

5-50 years
50-100 years
100-500 years

Lanthanides *	58 <b>Ce</b> 140.9077	59 <b>Pr</b> 144.24	60 <b>Nd</b> (145)	61 <b>Pm</b> 150.36	62 <b>Sm</b> 151.964	63 <b>Eu</b> 157.25	64 <b>Gd</b> 158.9253	65 <b>Tb</b> 158.9253	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.9303	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.9342	70 <b>Yb</b> 173.04	71 <b>Lu</b> 174.967
Actinides ‡	90 <b>Th</b> 232.0381	91 <b>Pa</b> 231.0289	92 <b>U</b> 238.0289	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)

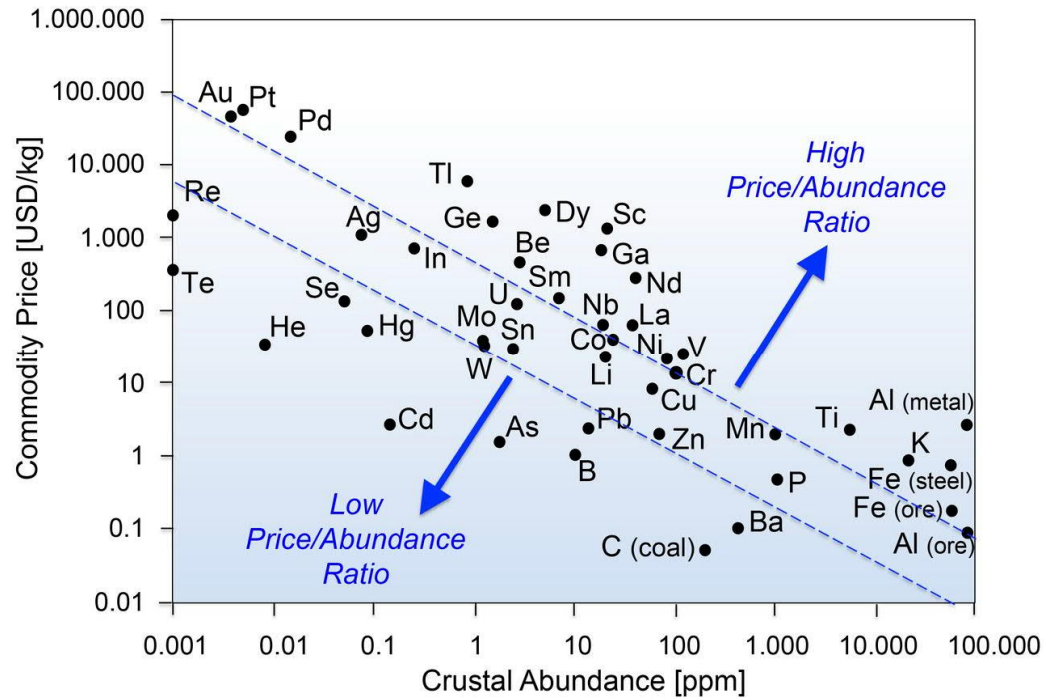


## London metal exchange

	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: often affected by fashion, speculation or politics besides the rarity

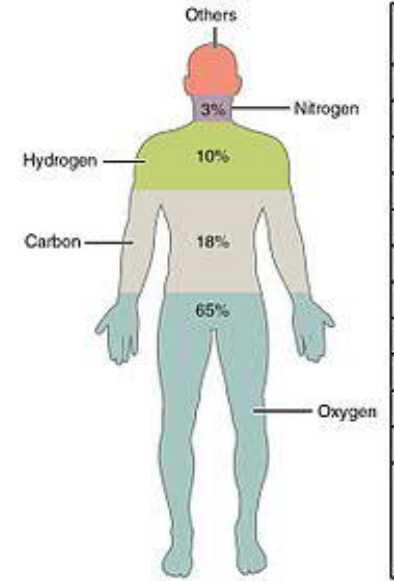


# CRITICAL for Health & Wellbeing

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

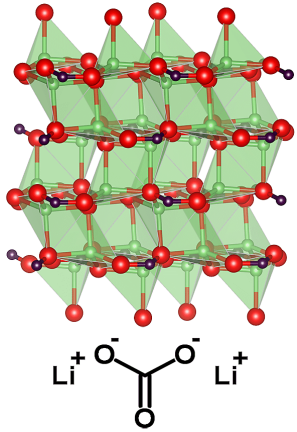


The four organic basic elements    Quantity elements    Essential trace elements    Possible structural or functional role in mammals

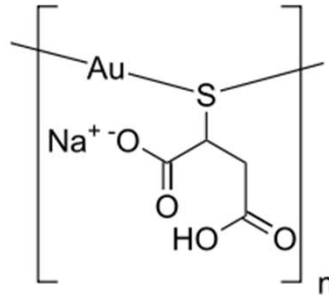


Supplement industry: \$5 billion in sales

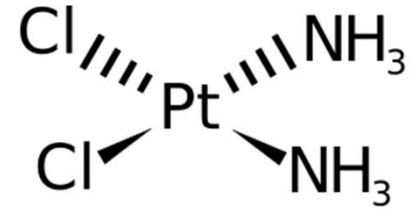
# CRITICAL as MEDICINE



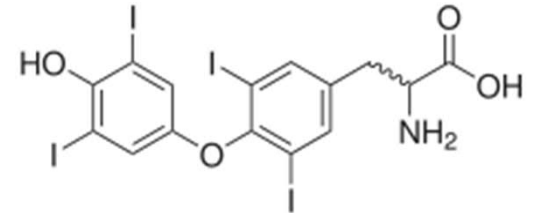
**Li<sub>2</sub>CO<sub>3</sub>** for depression



**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

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													

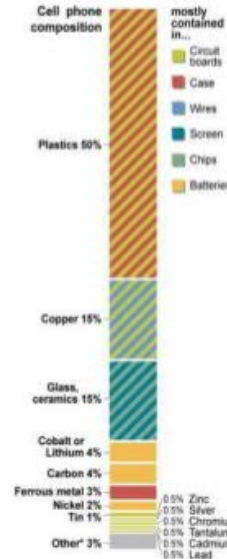
Elements used in the production of components for computers

# 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

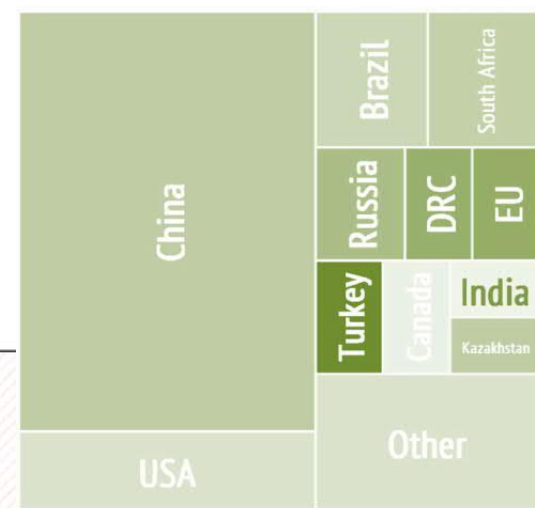


Courtesy of Dr Mike Pitts  
Sustainability Manager

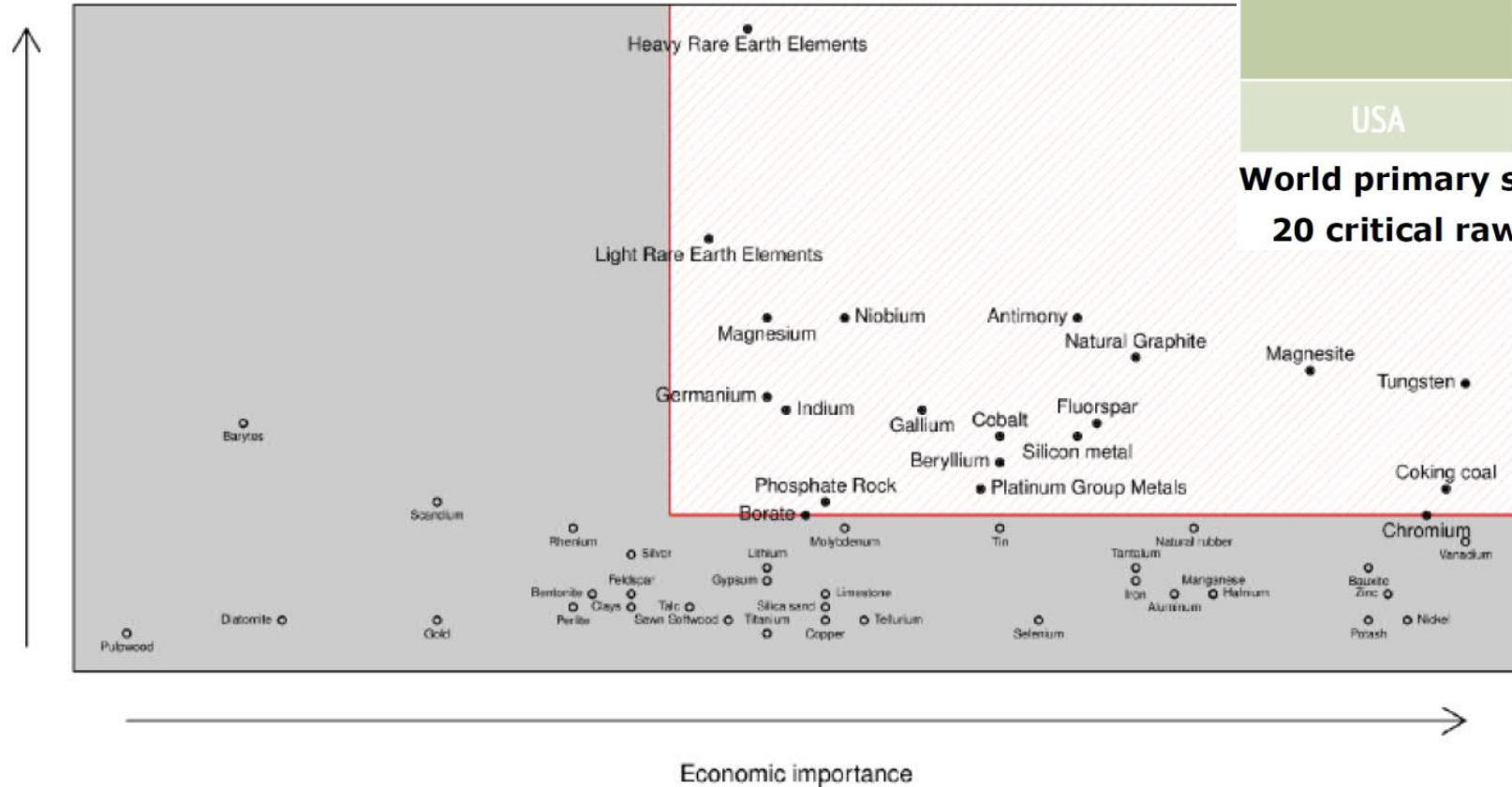
# CRITICAL RAW MATERIALS for EU

<http://ec.europa.eu/DocsRoom/documents/10010/attachments/1/translations>

<http://ec.europa.eu/DocsRoom/documents/11911/attachments/1/translations/en/renditions/pdf>

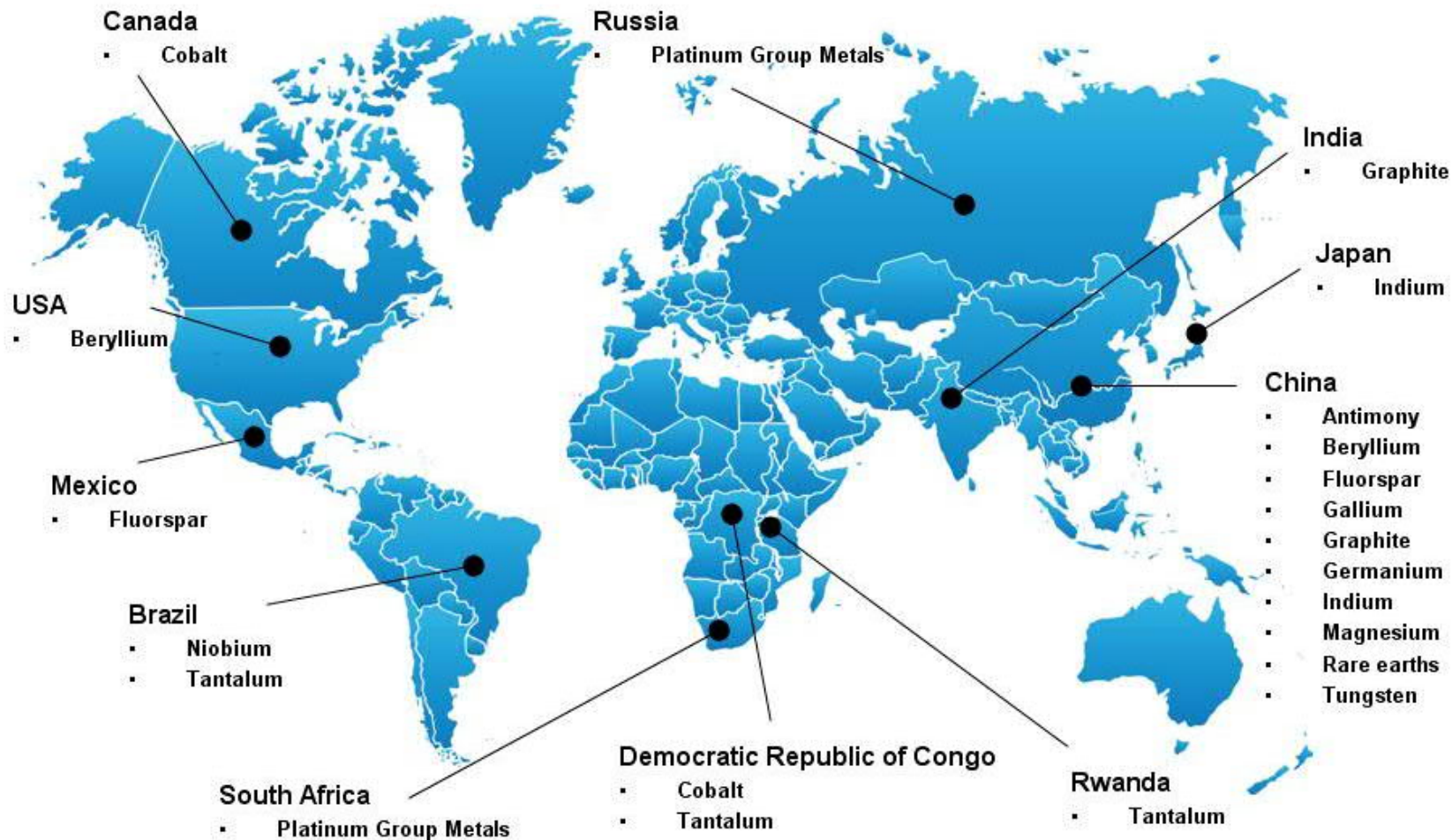


**World primary supply of the 20 critical raw materials**





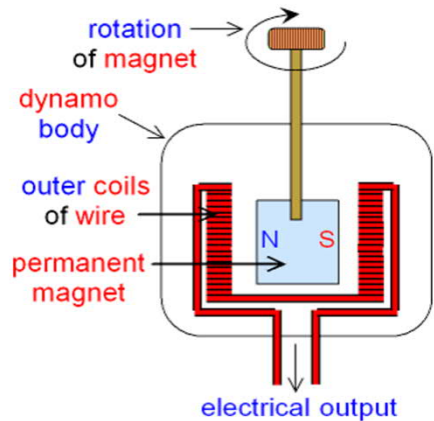
# Production concentration of critical raw mineral materials



# MATERIALS for ENERGY

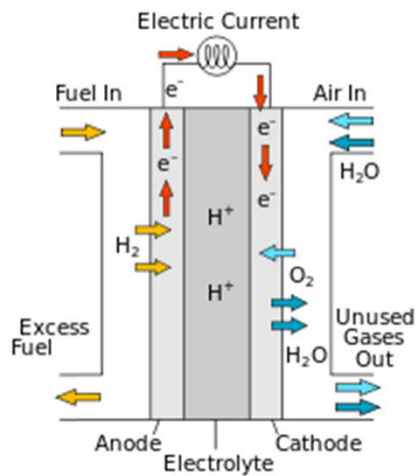
**TURBINES:** production of electricity from hydro, tidal, nuclear & fossil fuels

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



## FUEL CELLS

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

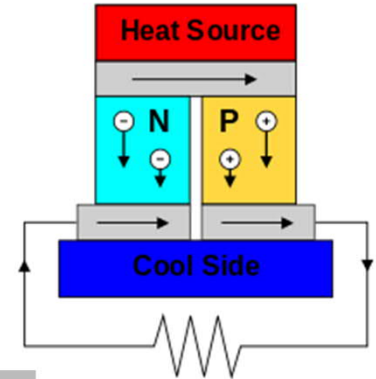


## PHOTOVOLTAICS

- In, Ga, etc. ...

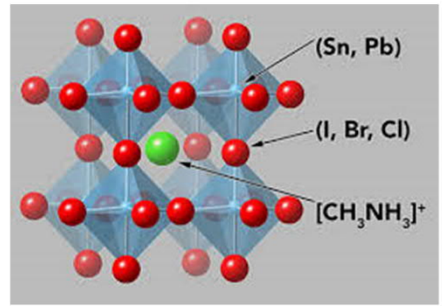
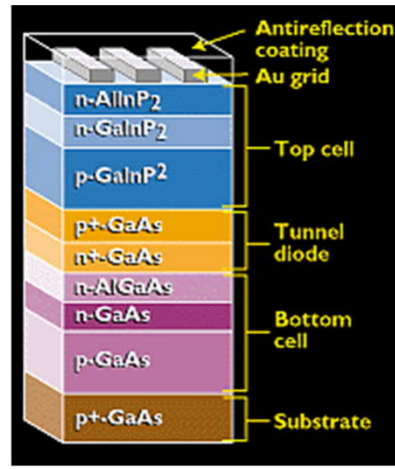
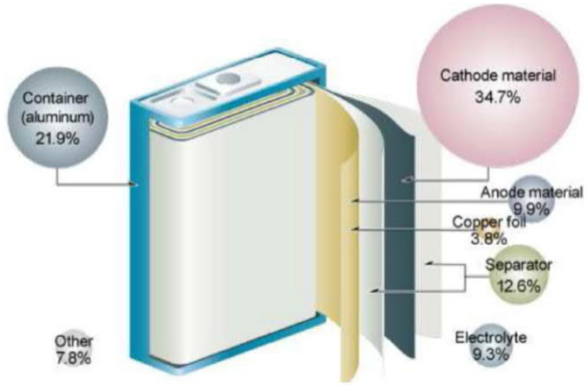
## THERMOELECTRICS

- Bi, Te, Se, Co, etc.



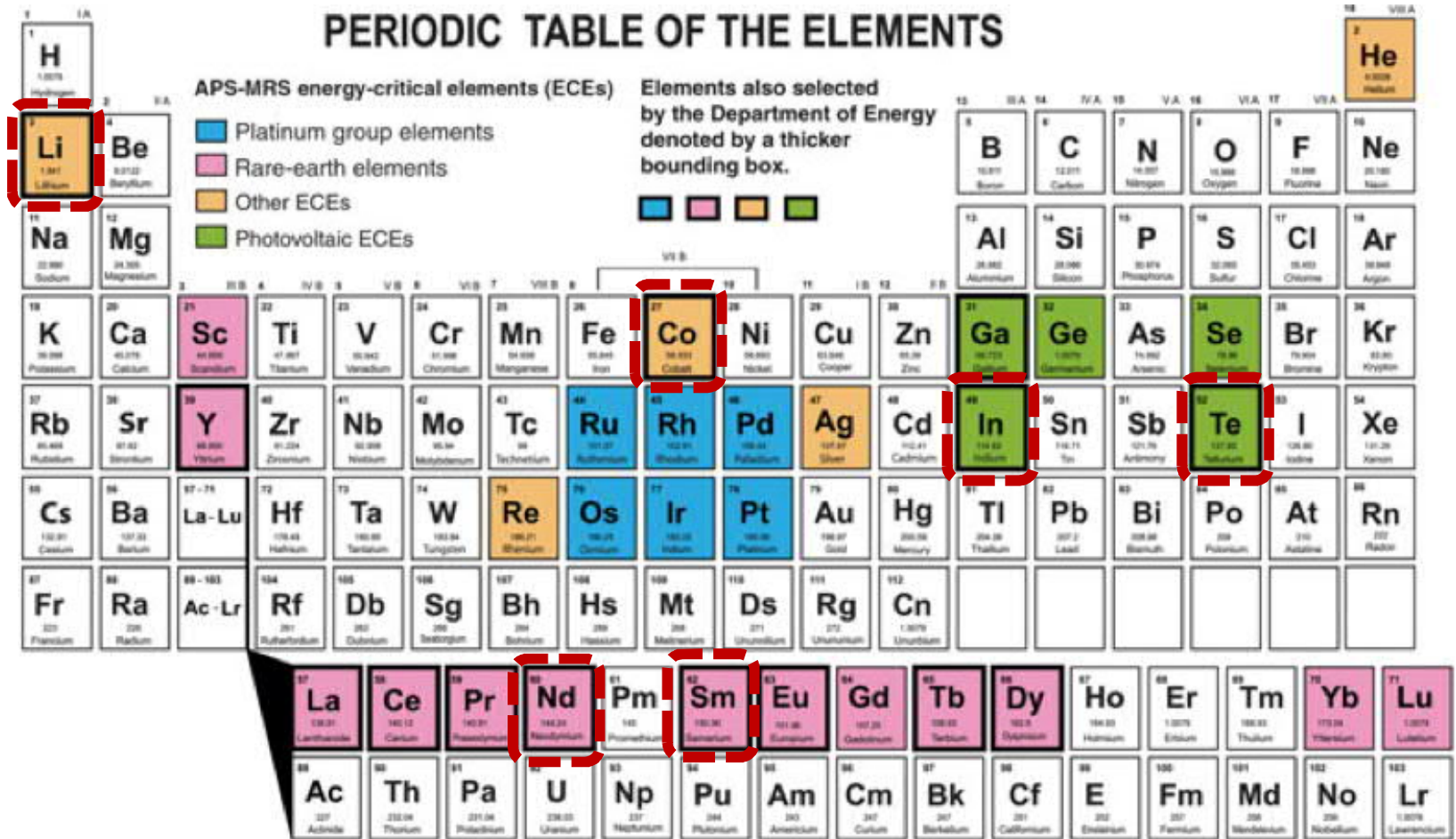
## BATTERIES

- Li, Co

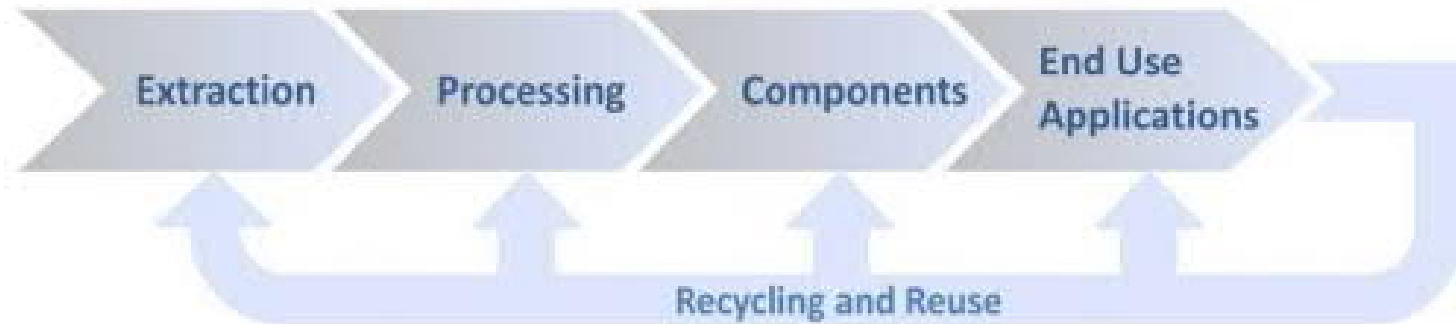




# ECE: Energy Critical Elements (by APS & MRS)



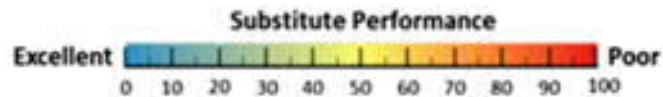
# REUSE & RECYCLING

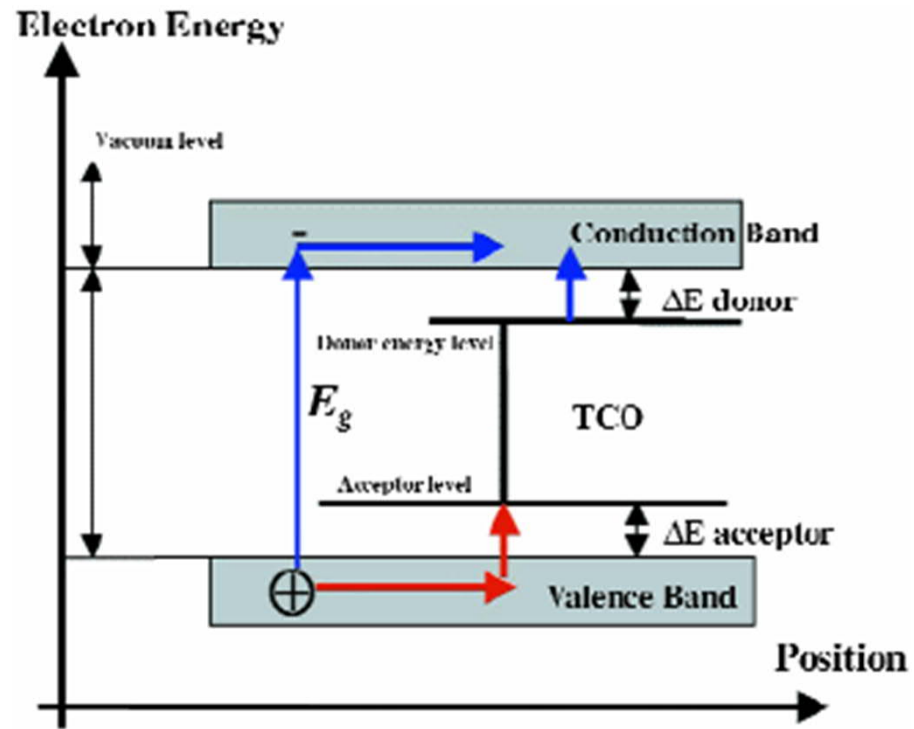


# SUBSTITUTIONS: Can it be done?

H																	He
Li 41	Be 63											B 41	C	N	O	F	Ne
Na	Mg 24											Al 44	Si	P	S	Cl	Ar
K	Ca	Sc 65	Ti 63	V 63	Cr 78	Mn 96	Fe 57	Co 54	Ni 62	Cu 70	Zn 38	Ga 38	Ge 44	As 38	Se 47	Br	Kr
Rb	Sr 78	Y 95	Zr 66	Nb 42	Mo 70	Tc	Ru 63	Rh 96	Pd 39	Ag 44	Cd 38	In 60	Sn 36	Sb 57	Te 38	I	Xe
Cs	Ba 63	*	Hf 38	Ta 41	W 53	Re 90	Os 38	Ir 69	Pt 66	Au 40	Hg 45	Tl 100	Pb 100	Bi 46	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

* Lanthanides	La 75	Ce 60	Pr 41	Nd 41	Pm	Sm 38	Eu 100	Gd 63	Tb 63	Dy 100	Ho 63	Er 63	Tm 88	Yb 88	Lu 63
** Actinides	Ac	Th 35	Pa	U 63	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr





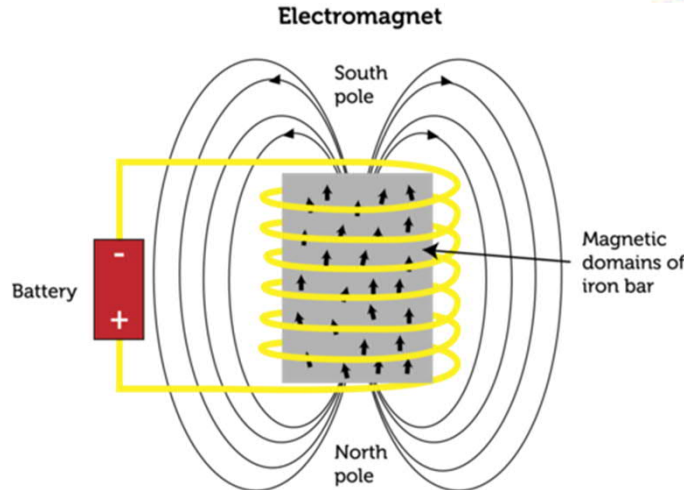
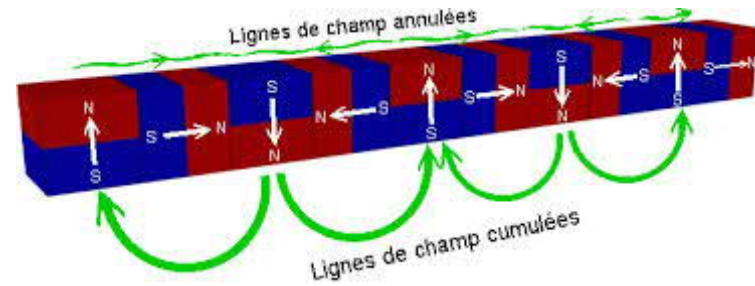
## TRANSPARENT CONDUCTING OXIDES (TCOs)

- ITO (In-Sn-O) is the current commercial leader, but the waste recovery is very much limited
- F-doped  $\text{SnO}_2$  is a good candidate
- Al-doped ZnO would be a highly sustainable replacement

# Strongest permanent magnet: $\text{Nd}_2\text{Fe}_{14}\text{B}$

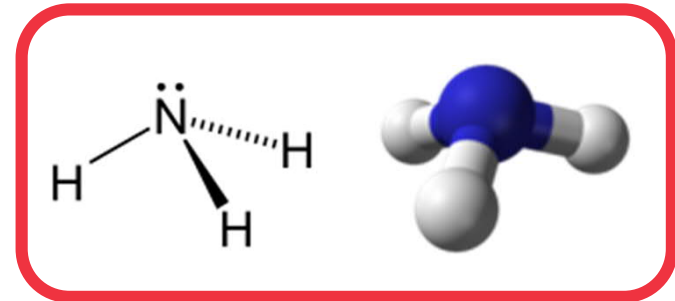
## “Non-Critical” ALTERNATIVES – Are there such ?

- $\text{AlNiCo}$ : “best of the rest”
- “Engineered”  $\text{Fe}_3\text{O}_4$
- Electromagnets

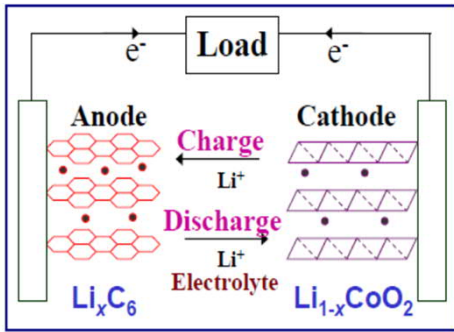


# Elemental substitutions for toxicity

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







**EC:** ethylene carbonate

**DEC:** dimethyl carbonate

**Cell:** (-) C | LiPF<sub>6</sub>-(EC+DEC) | LiCoO<sub>2</sub> (+)

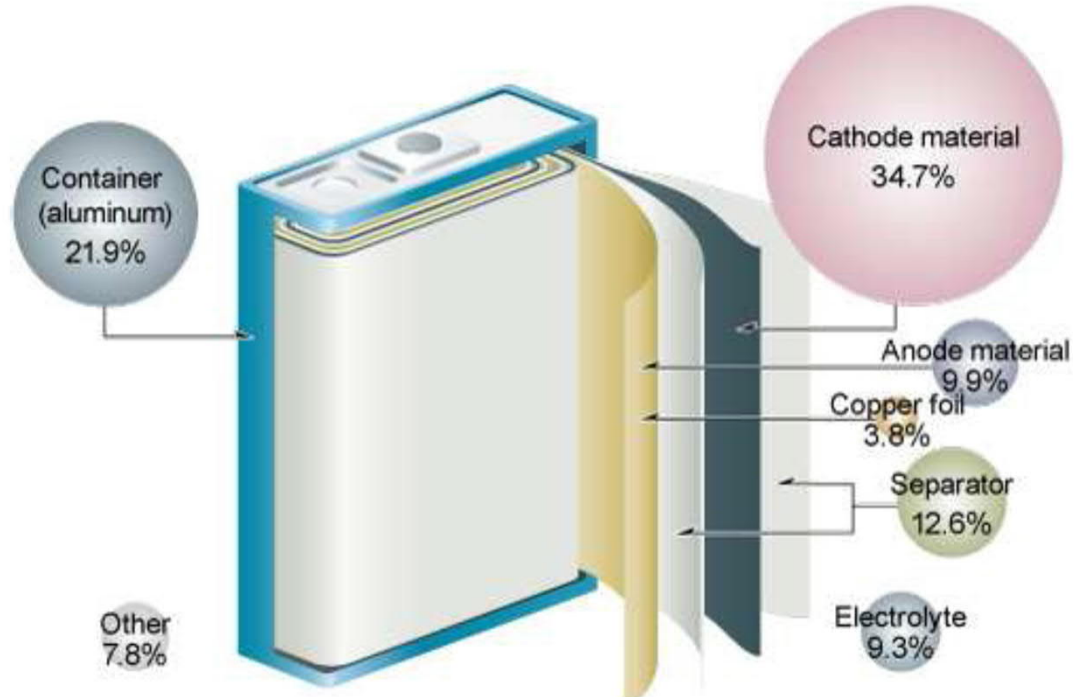
**Cathode:**  $\text{LiCoO}_2 \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$

**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: **LiCoO<sub>2</sub>**



# 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



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**

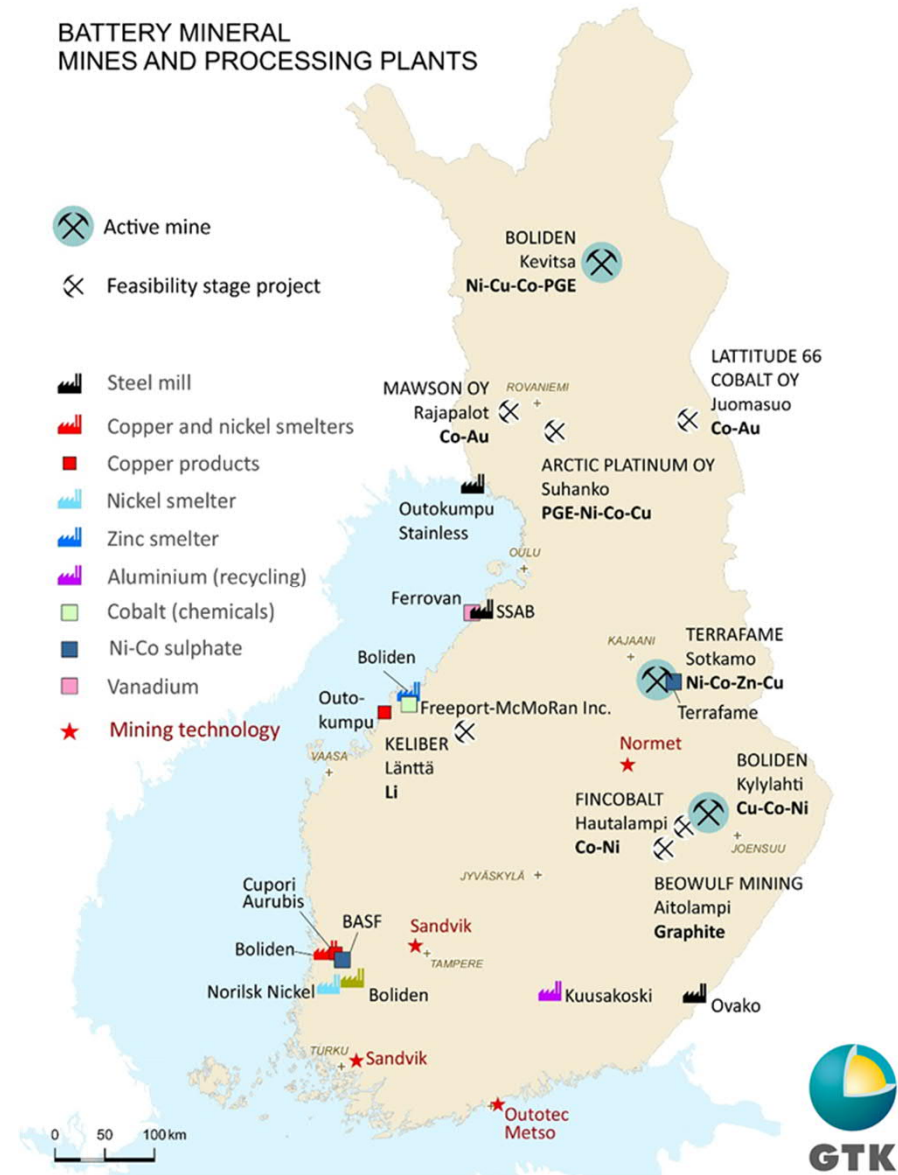


Cobolt mining place in Congo close  
to Kasulo. Valokuvat: Siddharth Kara

# Battery Minerals in FINLAND

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

“Ethical Cobalt/Metals”



Akku testaus



Freeport Cobalt



Akkujen kierrätys

Koboltin jalostus

AKKUSER

TiO<sub>2</sub> & Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>



Akkukemikaalit

SunChemical<sup>®</sup>

a member of the DIC group



Akkujen käyttäjä

Euroopan suurin litium esiintymä:  
LiAl(SiO<sub>3</sub>)<sub>2</sub> spodumeeni



Li-ioniakkujen tuotanto

walki

Elektrodien valmistus

A! Aalto-yliopisto  
Kemian korkeakoulu

Li-ioniakkujen materiaalitutkimus  
& akkumateriaalien kierrätys





**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  
LiCoO<sub>2</sub> 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



Aalto University, School of Chemical Engineering:

- Maarit Karppinen, Jari Koskinen, Rodrigo Serna, Mari Lundström, Tanja Kallio, Antti Karttunen, Kari Laasonen, Pertti Kauranen



VTT Technical Research Centre of Finland

- Tarja Laitinen, Päivi Kivikytö-Reponen, Pertti Koukkari



Univ. Helsinki, Consumer Society Research Centre / Univ. Cambridge

- Minna Lammi

Outotec



BOLIDEN



KOKKOLAN KAUPUNKI  
KARLEBY STAD



KULUTTAJALIITTO  
KONSUMENTFÖRBUNDET



Freeport  
Cobalt



PORI

Harjavalta  
Myötävärässä menestykseen

Ympäristööllisuus ja -palvelut  
The Federation of Finnish  
Technology  
Industries



**A!** Aalto University  
School of Chemical  
Technology

  
Ministry of Economic Affairs  
and Employment of Finland

  
Ympäristöministeriö  
Miljöministeriet  
Ministry of the Environment

  
Puolustusministeriö  
Försvarsministeriet  
Ministry of Defence

  
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MINISTRY OF AGRICULTURE AND FORESTRY

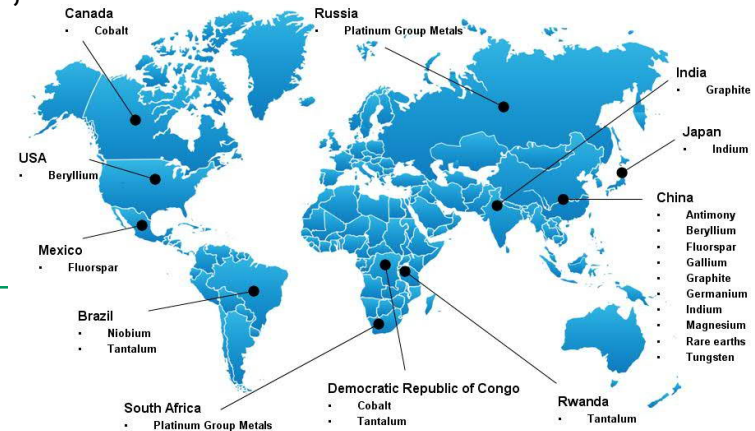
SITRA

  
RawMaterials

# Background & Motivation for CloseLoop

- **High-added-value Materials** are crucially needed in the Modern Society (ICT, transportation, renewable energy, *etc.*)
- Current Materials & Products are **designed for high performance, NOT for easy reuse or recycling**
- EU has listed 20 **Critical Raw Materials (CRMs)** with a high impact on the society but a high risk of supply shortage
- Currently the **recycling rates** for CRMs are **very low**
- Material substituents are searched for the CRMs, **BUT recycling of the new materials** should be considered as well

Production concentration of critical raw mineral materials



# CloseLoop Stakeholders

Harjavalta

*Myötävirrassa menestykseen*

**KUUSAKOSKI**  
RECYCLING

Freeport **Cobalt**

**REC**  
ALKALINE

**BOLIDEN**



**NORILSK NICKEL**

**Picodeon**  
Surface Freedom™

Fuel cell technology  
**elcogen**

**Puolustusministeriö**  
Försvarsministeriet  
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**YTP**

Ympäristöteollisuus ja -palvelut

**Outotec**



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KARLEBY STAD

**ESPOO**  
ESBO

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**Industries**

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**SITRA**

**CLOSELOOP**

<http://closeloop.fi/>

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.

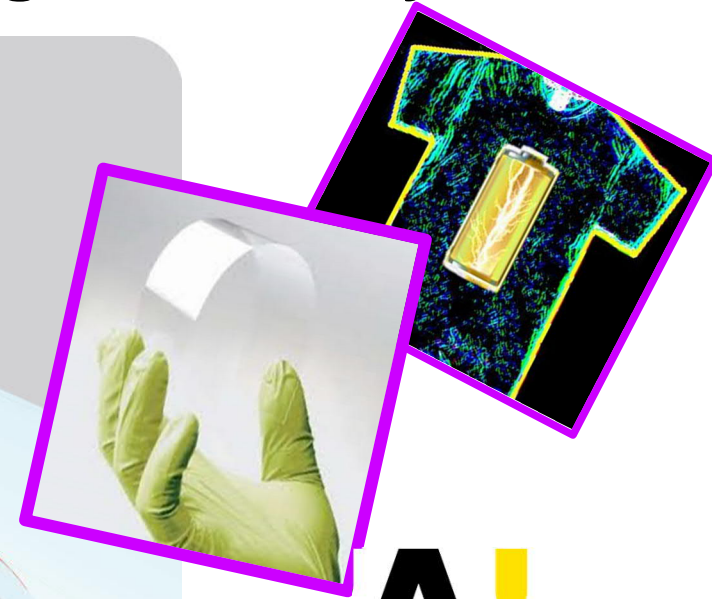
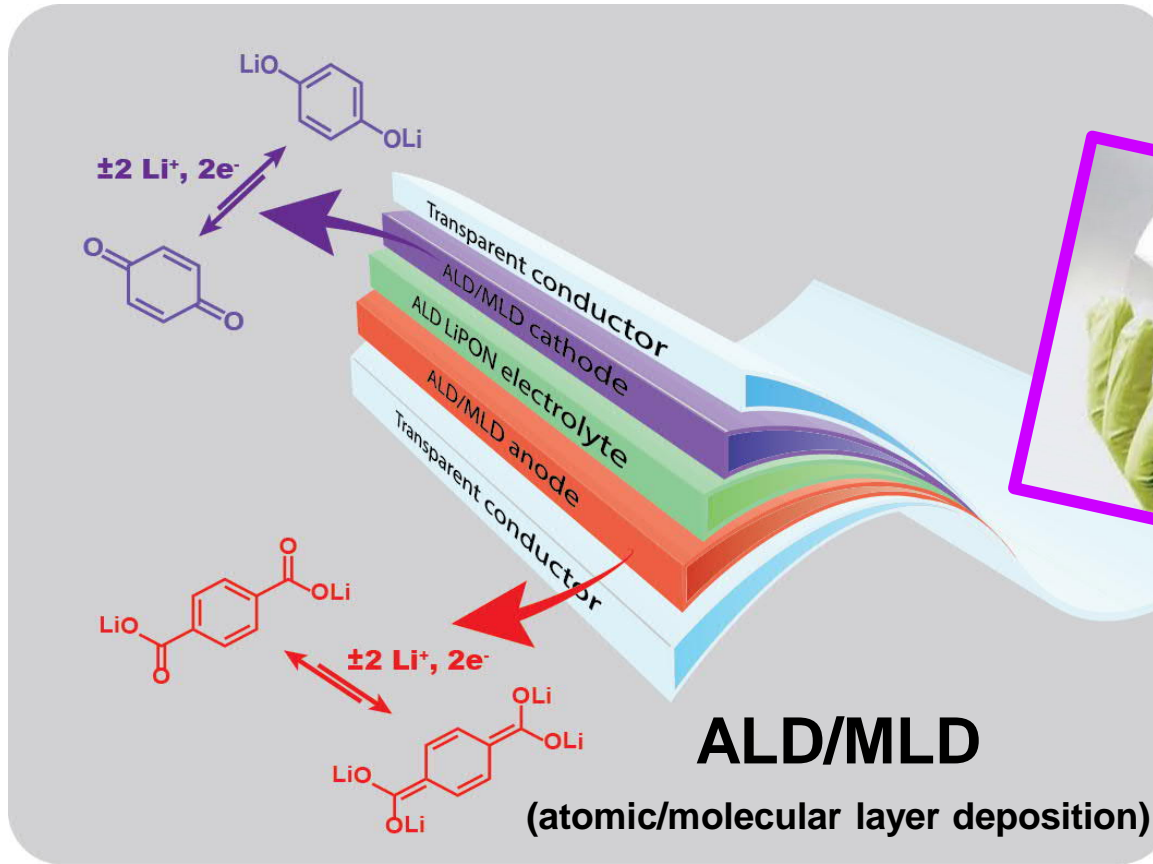
Due to the rapidly growing demand for electric cars, the recycling of battery raw materials and equipment will become ever more important. The European Commission has compiled a

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).