

HUNTING THE ELEMENTS OF THE PERIODIC TABLE ON SPACESHIP EARTH

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EuCheMS

Brussels, September 22, 2015

PERIODIC TABLE

– The ordinary picture –

Periodic Table of the Elements

Legend:

- Metals (Blue)
- Transition Elements (Yellow)
- Radioactive (Red)
- Nonmetals (Pink)
- Lanthanide Series (Green)
- Synthetic (Light Blue)
- Noble Gases (Orange)
- Actinide Series (Purple)
- Atomic weight of the most stable isotope (in parentheses)

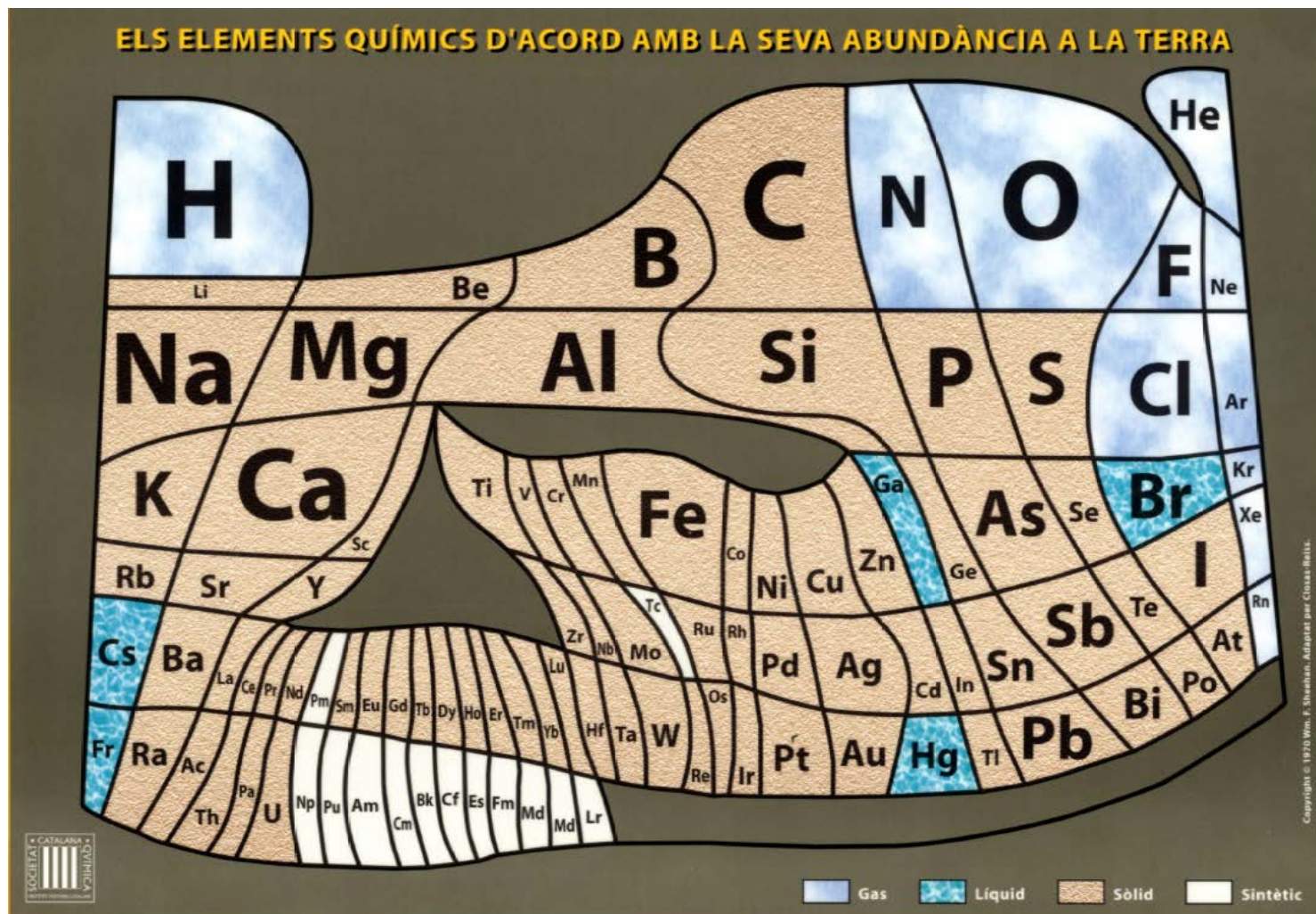
Callout for Oxygen (O):

- Group notation: VIA 16
- Atomic Number: 8
- Number of electrons in each shell: 2, 6
- Symbol: O
- Name: Oxygen
- Atomic Mass: 15.9994
- Period: 2

IA 1 H Hydrogen 1.00784																	VIIIA 18 He Helium 4.00206											
2 Li Lithium 6.941	IIA 4 Be Beryllium 9.012182											IIIA 5 B Boron 10.811	IVA 6 C Carbon 12.011	VA 7 N Nitrogen 14.00674	VIA 8 O Oxygen 15.9994	VIIA 9 F Fluorine 18.9984	X 10 Ne Neon 20.1797											
3 Na Sodium 22.98977	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.9736	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948											
4 K Potassium 39.0983	20 Ca Calcium 40.078	IIIB 3 Sc Scandium 44.9559	IVB 4 Ti Titanium 47.867	VB 5 V Vanadium 50.9415	VIB 6 Cr Chromium 51.9961	VII B 7 Mn Manganese 54.93805	VIII 8 Fe Iron 55.845	VIII 9 Co Cobalt 58.93320	VIII 10 Ni Nickel 58.934	IB 11 Cu Copper 63.546	12 Zn Zinc 65.39	13 Ga Gallium 69.723	14 Ge Germanium 72.61	15 As Arsenic 74.92159	16 Se Selenium 78.96	17 Br Bromine 79.904	18 Kr Krypton 83.80											
5 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29											
6 Cs Cesium 132.9054	56 Ba Barium 137.327	57-71 La-Lu Lanthanide Series										72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)		
7 Fr Francium (223)	88 Ra Radium 226.025	89-103 Ac-Lr Actinide Series										104 Unq Unnilquadium (261)	105 Unp Unnilpentium (262)	106 Unh Unnilhexium (263)	107 Uns Unnilseptium (262)	108 Uno Unniloctium (265)	109 Uue Unnilennium (266)	110 Uun Ununilium (269)	111 Uuu Ununium (272)									
		57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.9303	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967												
		89 Ac Actinium 227.028	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.048	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)												

PERIODIC TABLE

– The quantitative picture –



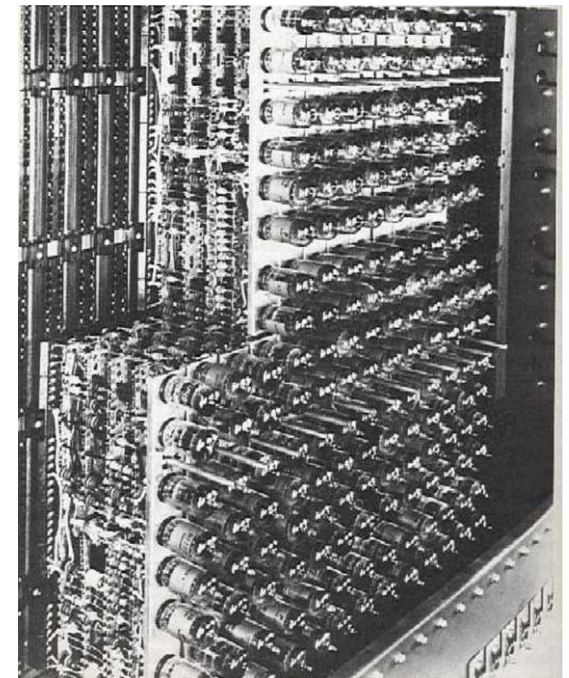
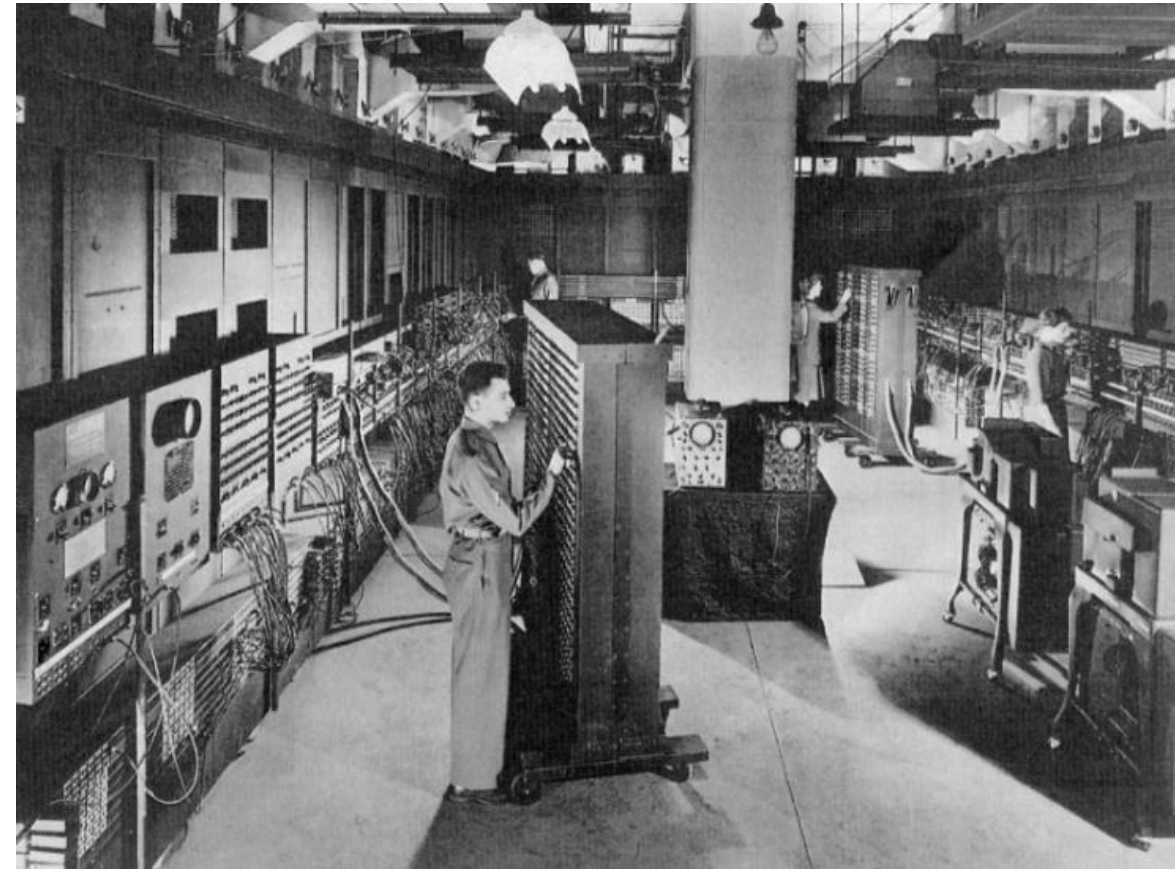
DEMATERIALIZISATION



ENIAC

the first electronic computer (1944)

- Weight: ≈ 30 t
- Valves: 19 000
- Consumption: 200 000 W



THIS COMPUTER



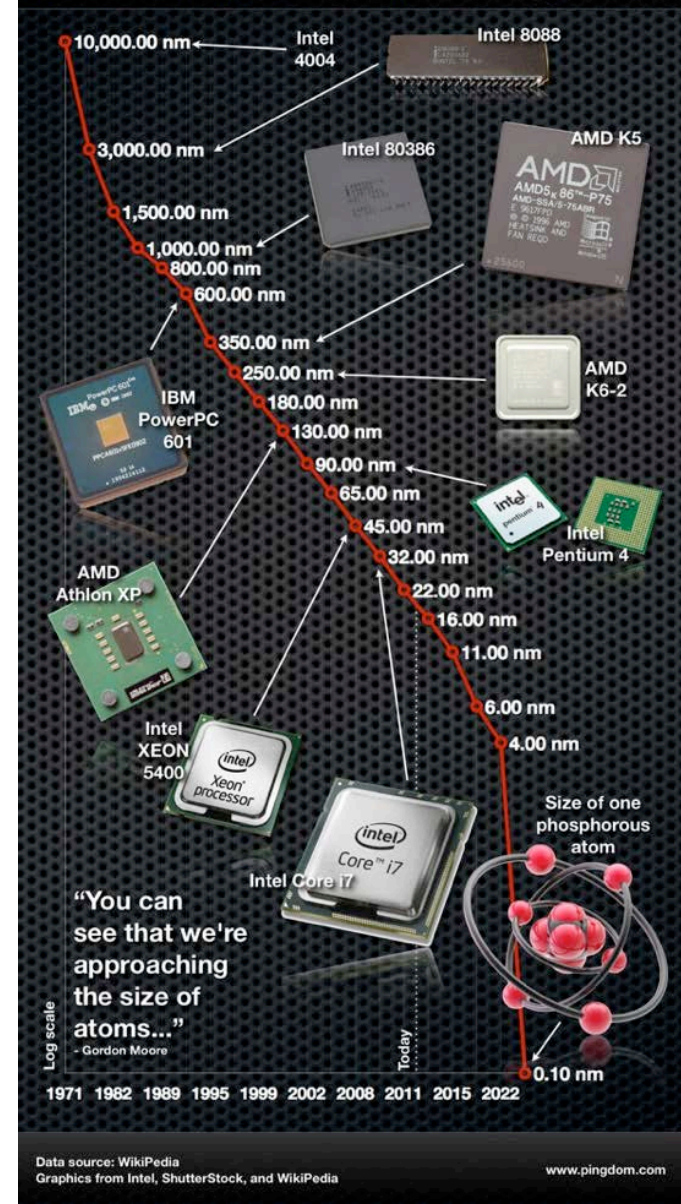
Weight: 1.5 kg

Consumption: 30 W

1.3 billions of transistors

Average dimension: 22 nm

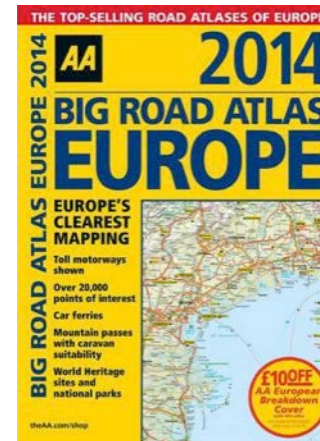
How small can a transistor be? The evolution of microprocessor manufacturing processes



THE CHAMPION OF DEMATERIALIZATION



129 grams



THE PRICE TO PAY: A MORE INTENSIVE HUNTING OF THE PERIODIC TABLE

2015

Over **40** elements in a mobile phone

1990

Less than **20** elements in an entire house

ELEMENTS OF A SMARTPHONE

ELEMENTS COLOUR KEY: ● ALKALI METAL ● ALKALINE EARTH METAL ● TRANSITION METAL ● GROUP 13 ● GROUP 14 ● GROUP 15 ● GROUP 16 ● HALOGEN ● LANTHANIDE

SCREEN

In Indium
O Oxygen
Sn Tin

Indium tin oxide is a mixture of indium oxide and tin oxide, used in a transparent film in the screen that conducts electricity. This allows the screen to function as a touch screen.

Al Aluminium
Si Silicon
O Oxygen
K Potassium

The glass used on the majority of smartphones is an aluminosilicate glass, composed of a mix of alumina (Al₂O₃) and silica (SiO₂). This glass also contains potassium ions, which help to strengthen it.

Y Yttrium
La Lanthanum
Tb Terbium
Pr Praseodymium
Eu Europium
Dy Dysprosium
Gd Gadolinium

A variety of Rare Earth Element compounds are used in small quantities to produce the colours in the smartphone's screen. Some compounds are also used to reduce UV light penetration into the phone.

BATTERY

Li Lithium
Co Cobalt
C Carbon
Al Aluminium
O Oxygen

The majority of phones use lithium ion batteries, which are composed of lithium cobalt oxide as a positive electrode and graphite (carbon) as the negative electrode. Some batteries use other metals, such as manganese, in place of cobalt. The battery's casing is made of aluminium.

ELECTRONICS

Cu Copper
Ag Silver
Au Gold
Ta Tantalum

Copper is used for wiring in the phone, whilst copper, gold and silver are the major metals from which microelectrical components are fashioned. Tantalum is the major component of micro-capacitors.

Ni Nickel
Dy Dysprosium
Pr Praseodymium
Tb Terbium
Nd Neodymium
Gd Gadolinium

Nickel is used in the microphone as well as for other electrical connections. Alloys including the elements praseodymium, gadolinium and neodymium are used in the magnets in the speaker and microphone. Neodymium, terbium and dysprosium are used in the vibration unit.

Si Silicon
O Oxygen
Sb Antimony

Pure silicon is used to manufacture the chip in the phone. It is oxidised to produce non-conducting regions, then other elements are added in order to allow the chip to conduct electricity.

Sn Tin
Pb Lead

Tin & lead are used to solder electronics in the phone. Never lead-free solders use a mix of tin, copper and silver.

CASING

C Carbon
Mg Magnesium
Br Bromine
Ni Nickel

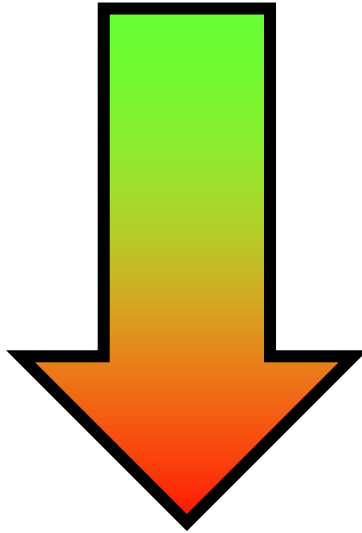
Magnesium compounds are alloyed to make some phone cases, whilst many are made of plastics. Plastics will also include flame retardant compounds, some of which contain bromine, whilst nickel can be included to reduce electromagnetic interference.

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Source: <http://www.compoundchem.com>

DEMATERIALIZATION



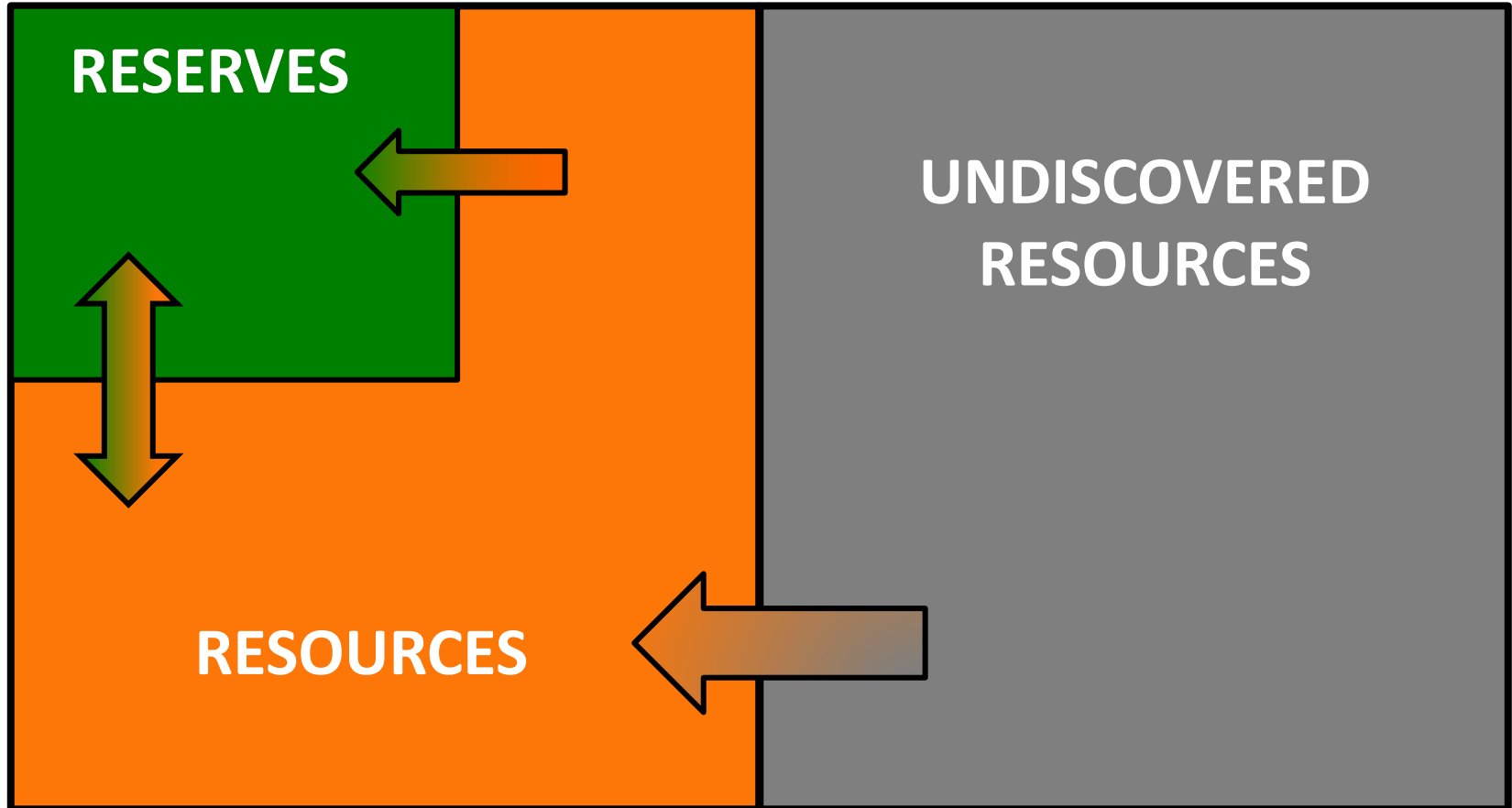
MATERIAL INTENSIFICATION

OUR “MINE”: A TINY SPACESHIP EARTH



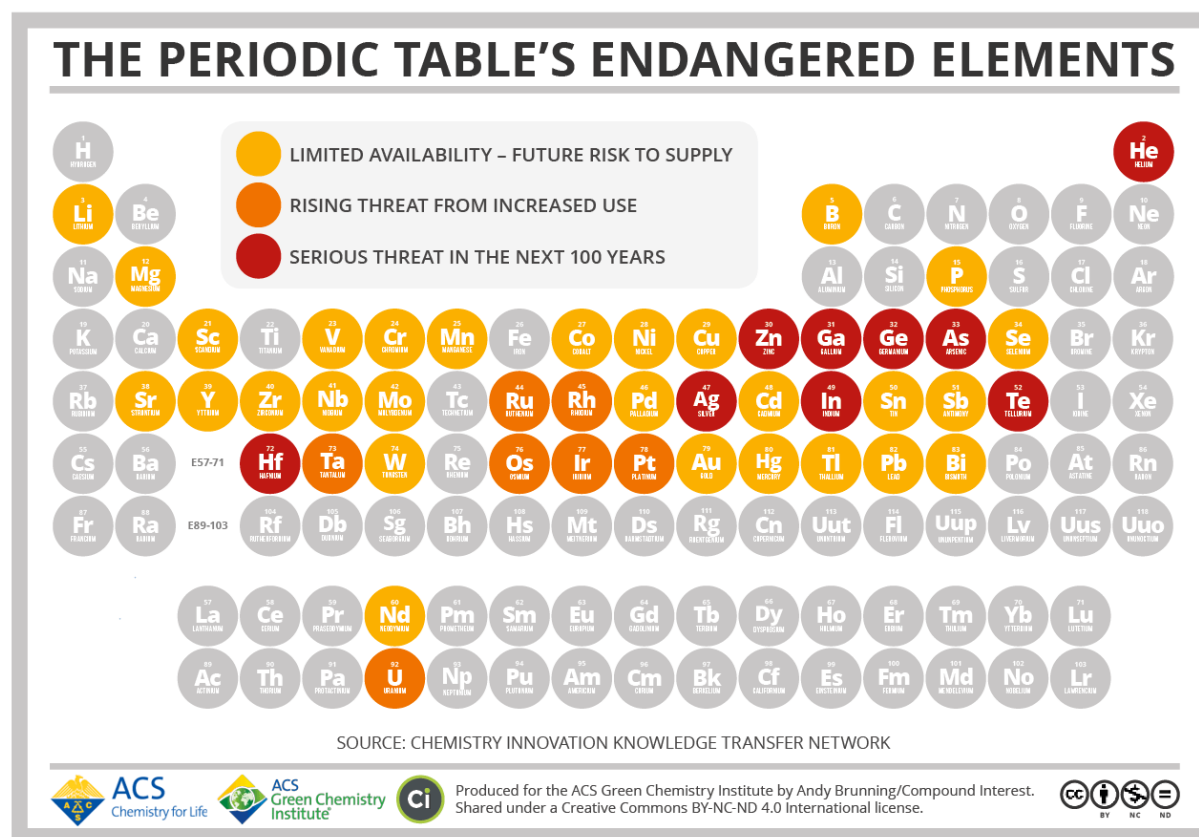
We can dig
down to about
5 km

MINERAL “RESOURCES” AND “RESERVES”

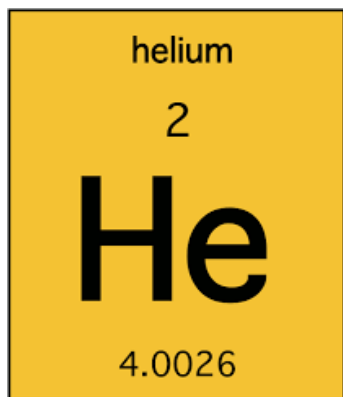


Critical Raw Materials for the EU, The European Commission, 2010

ENDANGERED ELEMENTS: SELECTED EXAMPLES

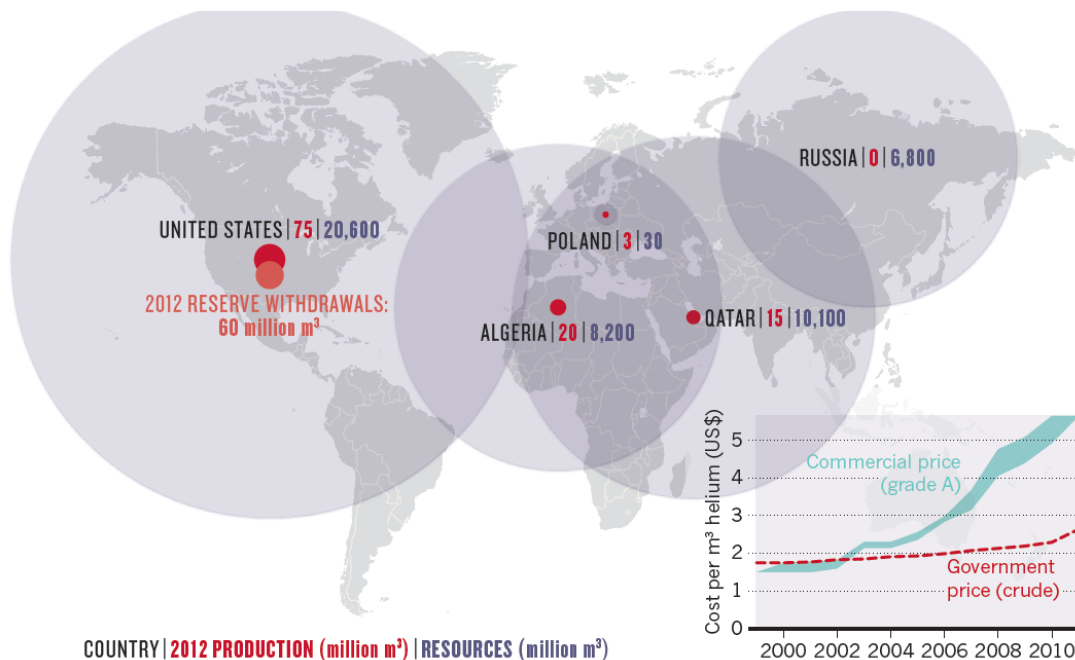


HELIUM

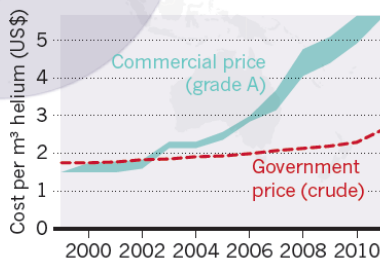


GAS – 2nd most abundant element of the Universe, but very rare on Earth, where it escapes from (0.0005% of the volume of the atmosphere)

Main source: natural gas wells (from nuclear decay)

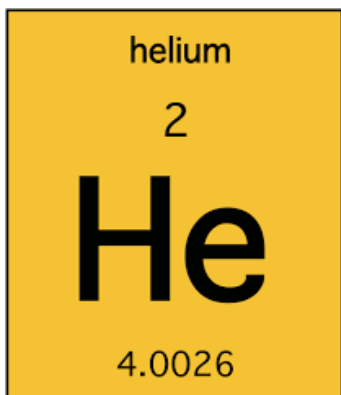


US has been always the dominant world market player, through its Federal Helium Reserve in Texas



Nature 2013, 497, 168

HELIUM: Absolutely unique physical properties

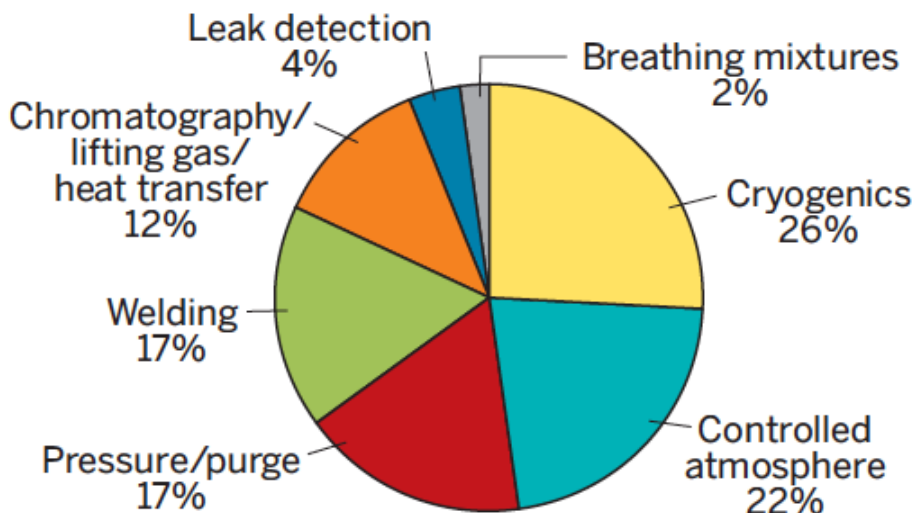


Boiling point: $-268,93^{\circ}\text{C}$ (4.22 K)

Melting point: $-272,20^{\circ}\text{C}$ (0.94 K)

Below 2K, it enters a superfluid state with no apparent viscosity and extremely high thermal conductivity.

Perfect for extreme cryogenic uses



Demand soaring, supply decreasing

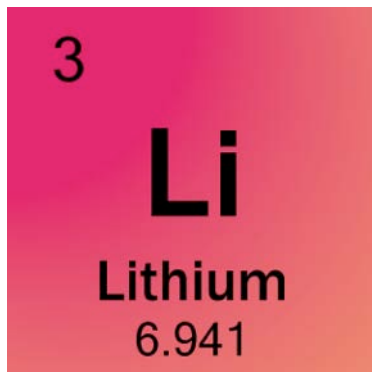
Price 2012: **7 \$/L** ; Price 2015: **17 \$/L**

BIG problem in many research labs and technological facilities around the world

Chem. Eng. News 2015, July 27

Chem. Eng. News 2013, Sept. 16

LITHIUM



METAL – very unstable in air and water.
Major producers: Australia, Chile and China.
Estimated world reserves: 13.5 Mton



The largest resource
in the world:
Salar de Uyuni, Bolivia
10,000 km²

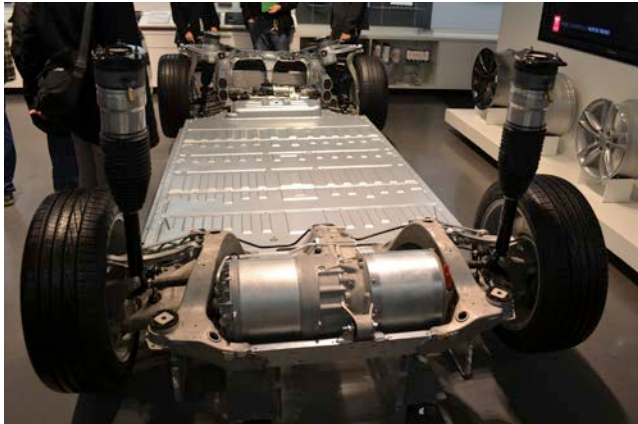
LITHIUM: demand projected to explode

3

Li

Lithium
6.941

The **lightest solid metal** with the **highest electrochemical potential**: high gravimetric and volumetric energy and power density
IDEAL FOR BATTERIES



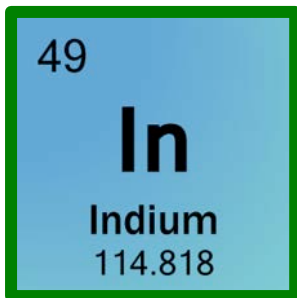
Cars sold per year worldwide: **70 millions**

If electric : **≈ 700 000 ton** of Li required

Current Li world production: **36 000 ton/y**
(USGS, 2014)

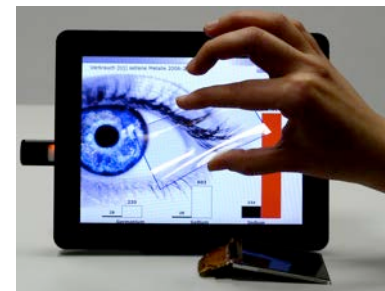
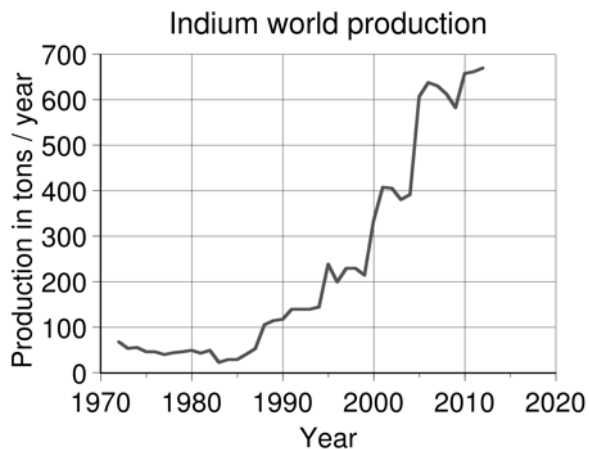
**Lithium is also needed for portable devices, ceramics, lubricants, alloys and ... Tritium (nuclear fusion).
RECYCLING WILL BE CRUCIAL (not difficult)**

INDIUM



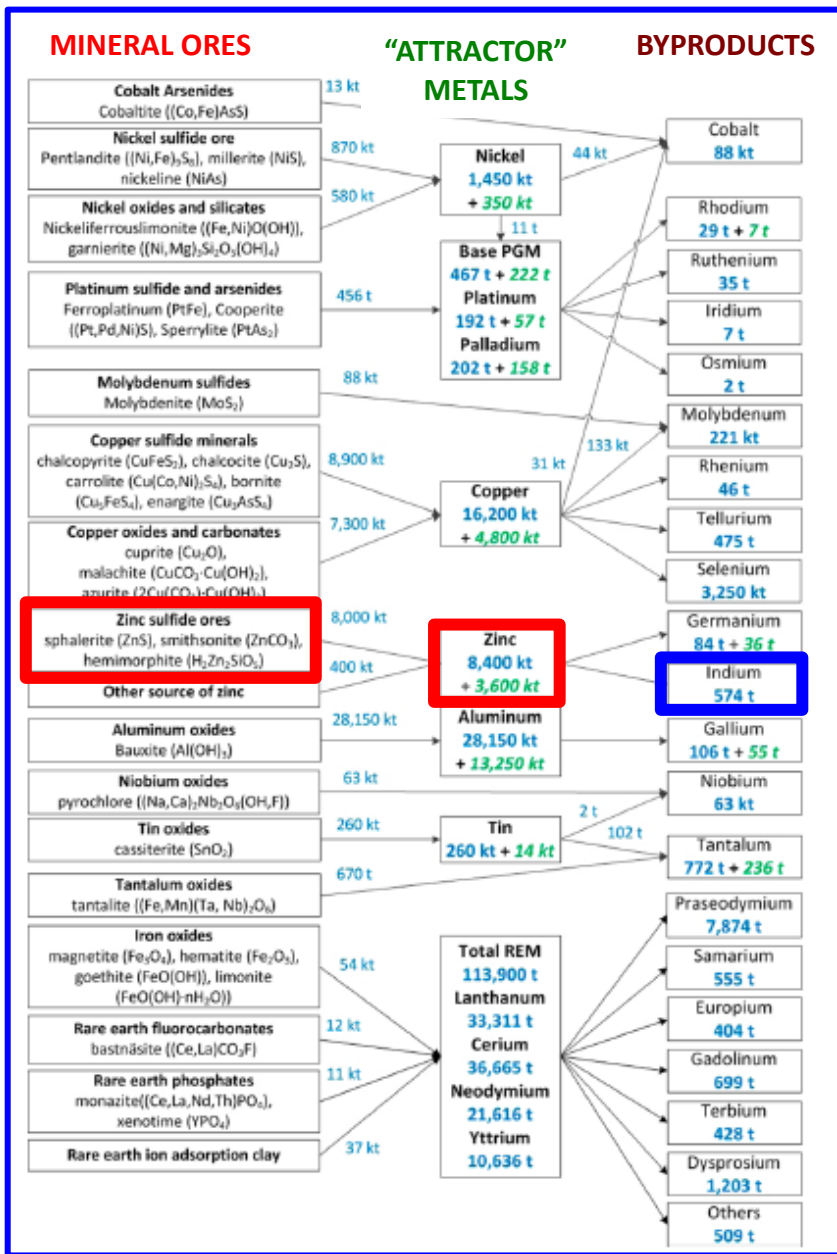
METAL – soft and stable in air and water. Major producers: China, South Korea and Japan. Estimated reserves: unknown (USGS, 2015)

Relatively useless until 20 years ago, then ...



Indium Tin Oxide (ITO)

Transparent, conductor, binds strongly to glass



INDIUM IS NOT OBTAINED DIRECTLY

ATTRACTOR METALS
(Pt, Pd, Cu, Zn, Al, Sn, La, Ce, Nd, Y)

"HITCHHIKERS"
(Co, Rh, Ru, Ir, Os, Mo, Re, Te, Se, Ge, In, Ga, Nb, Ta, heavy rare earth elements)



**Price volatility,
risk of uncontrolled
supply disruptions**

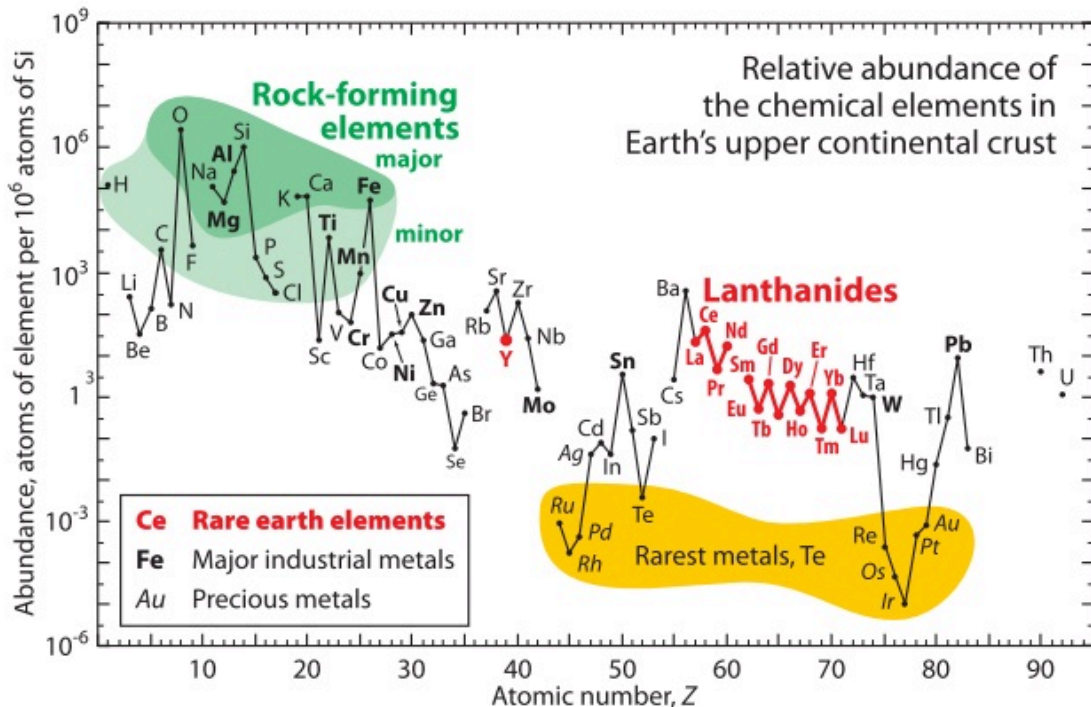
RARE EARTH ELEMENTS (REE)

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		1 H 1.008																	2 He 4.003
2		3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16	9 F 19	10 Ne 20.18
3		11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4		19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.9	36 Kr 83.8
5		37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6		55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209	84 Po (210)	85 At (210)	86 Rn (222)
7		87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (271)	111 Rg (272)	112 Uub (285)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (292)	117 Uus 0	118 Uuo 0
	6	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175				
	7	90 Th 232	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)				

Unique
MAGNETIC
PHOSPHORESCENT
OPTICAL
CATALYTIC
 properties

14 “LANTHANIDES” (no Pm) + Sc and Y

RELATIVE CONCENTRATION OF ELEMENTS (upper continental crust)



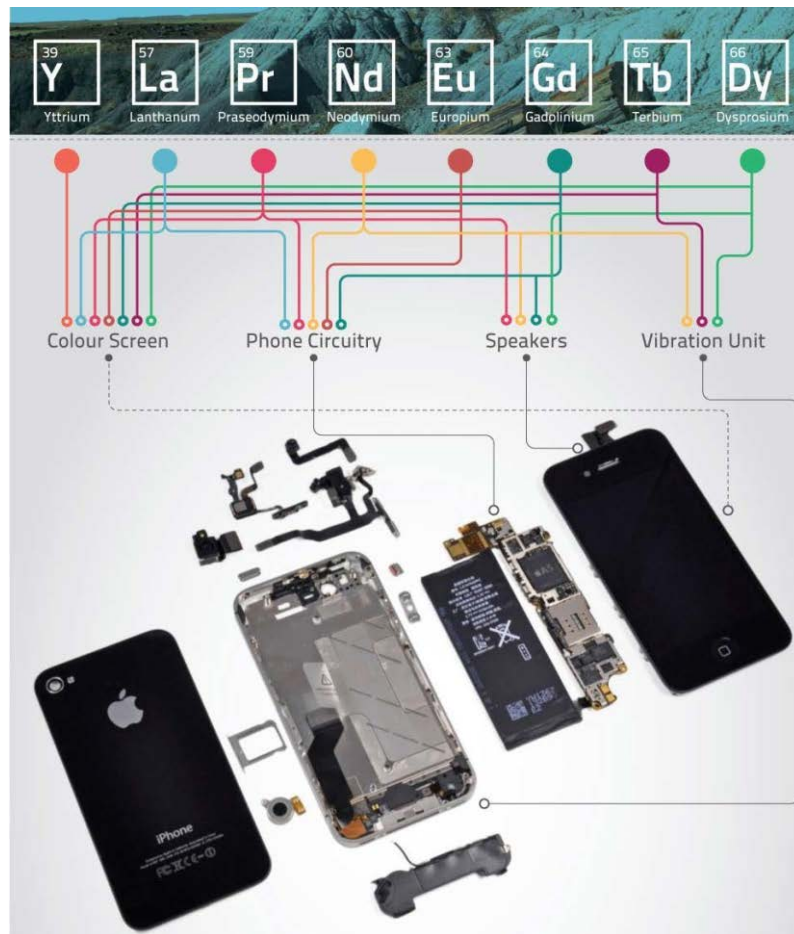
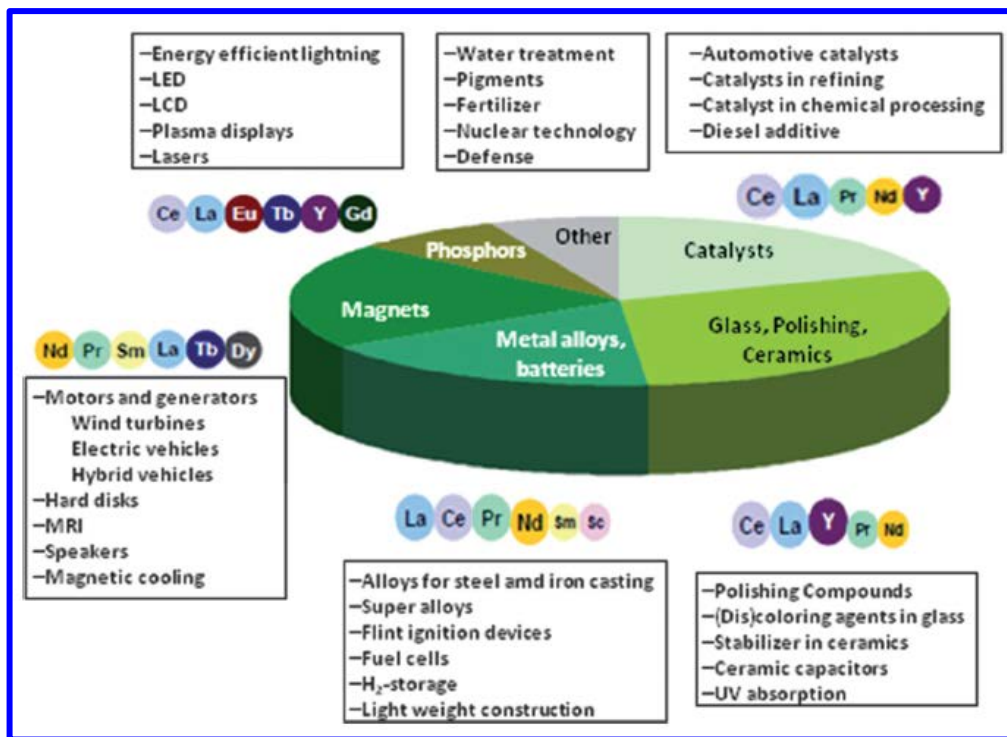
**REE ARE
NOT SO RARE
 BUT ARE RARELY
CONCENTRATED
ENOUGH TO SUPPORT
ECONOMICALLY
CONVENIENT
RECOVERY**

Light REE: Sc, La, Ce, Pr, Nd, Pm, Sm, Eu

Heavy REE: Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu ⇒ Typically more rare

REE: CRUCIAL FOR A NUMBER OF APPLICATIONS

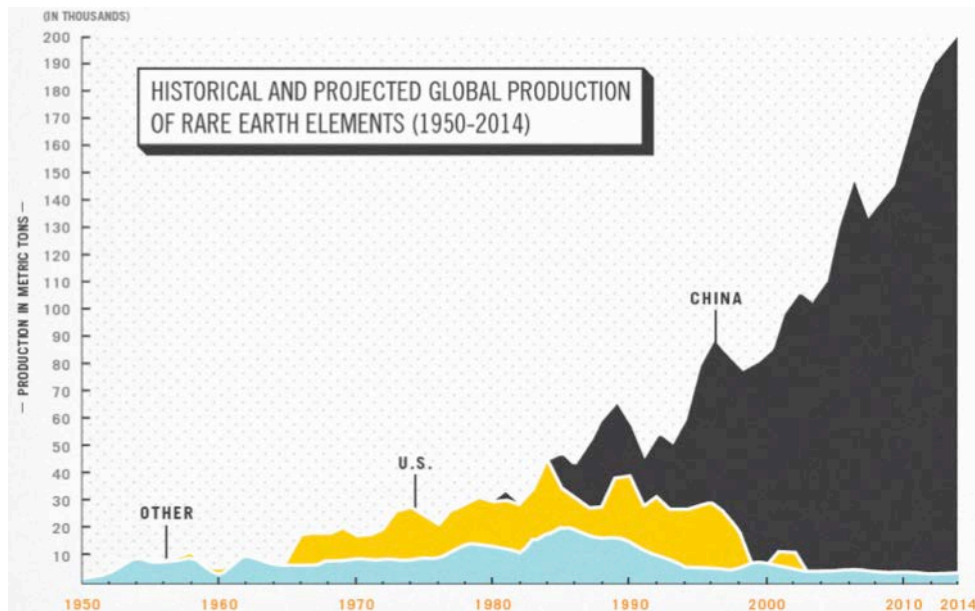
REE IN SMARTPHONES



ChemSusChem 2013, 6, 2045

<http://www.rareelementresources.com>

REE: THE CHINESE SUPPLY MONOPOLY



No good news
from U.S.

BUSINESS

Chem. Eng. News
2015, July 27, p. 36

THE STRUGGLE TO MINE RARE EARTHS

Molycorp faces operating and financial hurdles at the only U.S. RARE-EARTH MINE

MELODY M. BOMGARDNER, C&EN WEST COAST NEWS BUREAU

AS TWO FULL TOUR BUSES arrived at Molycorp's rare-earth mine in Mountain Pass, Calif., late last month, thick clouds cast merciful shade on the high desert. The mine is located about an hour southwest of Las Vegas, where the temperature was expected to reach 110 °F. Yet, a more ominous shadow lurked over the event: Four days earlier, Molycorp had filed for Chapter 11 bankruptcy.

The visitors were greeted by Jim Sims, Molycorp's head of communications. "The timing of this event is a little strange," he acknowledged, "but we are operational."

The state of operations at the mine is of great interest not just to Molycorp's credi-

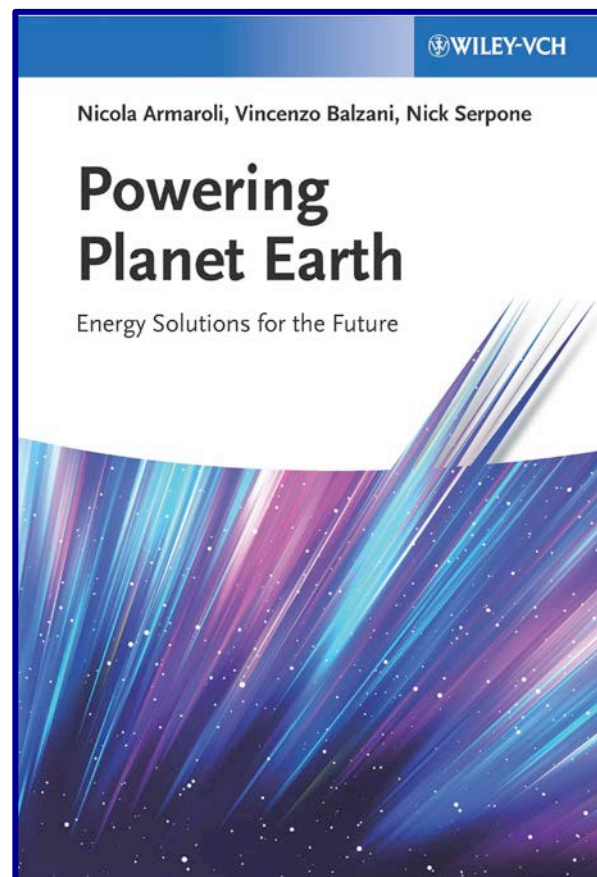
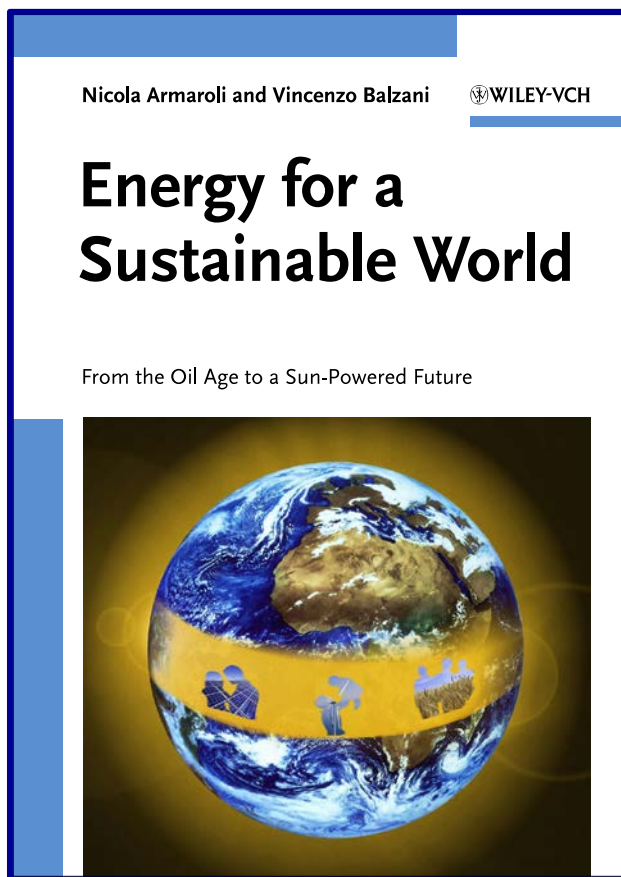
tors but also to manufacturers of products that contain rare earths such as electric vehicles, electronics, wind turbines, lighting, and batteries. Today, 90% of the world's rare earths are produced in China. It would be closer to 100% but for Molycorp's output of cerium, lanthanum, neodymium, and praseodymium oxides and carbonates.

China's near-monopoly gained widespread attention in 2010 when the country lowered export quotas for rare earths, causing prices to skyrocket. Starting in 2012, however, prices began to decline. In May, China did away with the quotas following a ruling from the World Trade Organization.

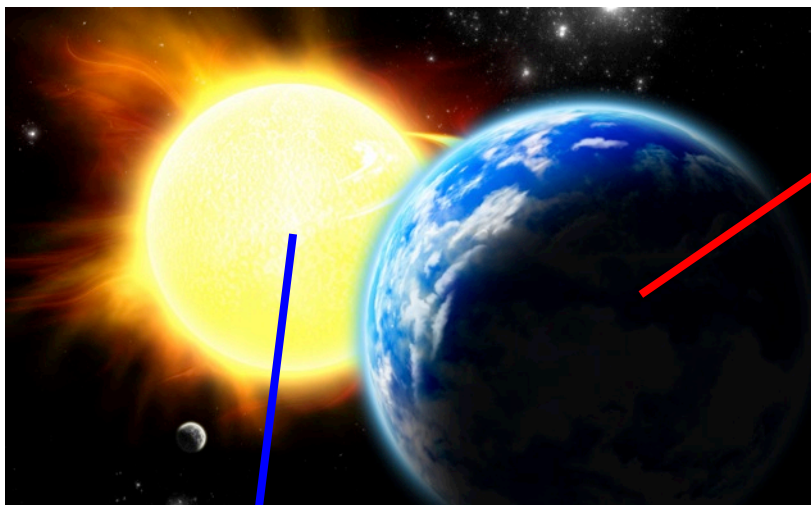


The price run-up spurred calls for development of rare earths from mines outside of China—in particular the Mountain Pass mine. But mining companies are now caught in a bind: They are working to increase output at a time when lower prices make it extremely difficult to turn a profit. Looking ahead, Molycorp will need to both increase production and obtain higher—or at least stable—prices to survive, goals that can be mutually exclusive in today's market, experts say.

ENDANGERED ELEMENTS AND THE TRANSITION TO A SUN-POWERED WORLD



FOR USING SOLAR ENERGY WE NEED PHOTONS AND ATOMS (*i.e.*, CHEMICAL ELEMENTS)



Photons are an overabundant
“extraterrestrial” input
amounting to THOUSANDS
of times our needs

We need CONVERTERS of solar energy,
made of “terrestrial” materials, which
are available in limited supply



RARE ELEMENTS IN RENEWABLE AND EFFICIENT ENERGY TECHNOLOGIES



**THIN FILM
PV PANELS:
Indium, Gallium,
Tellurium**



**Neodymium, Praseodymium,
Dysprosium**

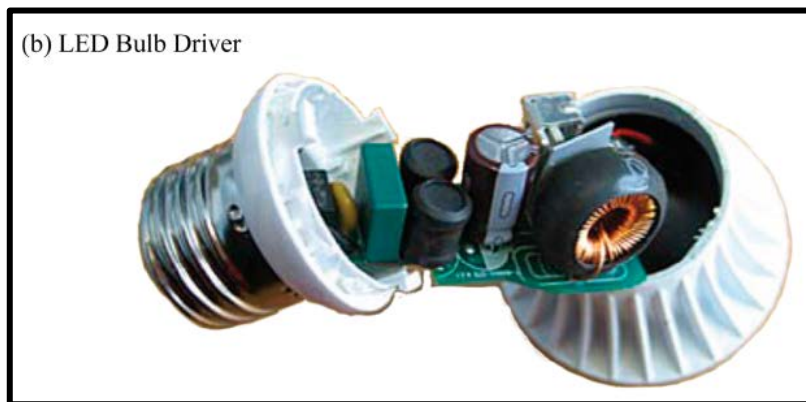
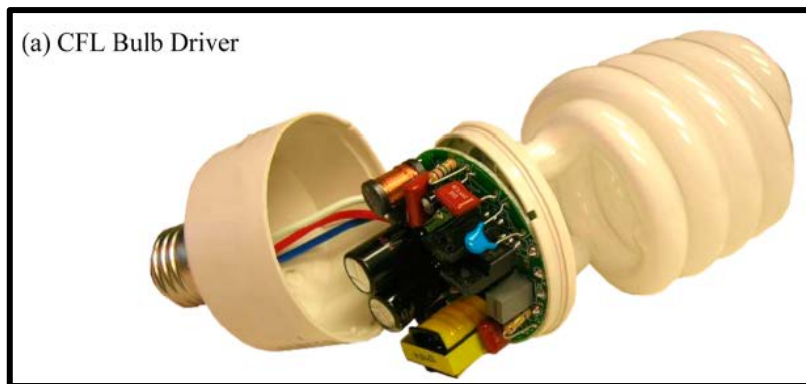


- Neodymium, Praseodymium
Dysprosium
- Lanthanum, Cerium; Lithium, Cobalt,



**Europium, Terbium,
Yttrium, Cerium**

LIGHTING EFFICIENCY COMES AT A PRICE



METAL CONTENT

Environ. Sci. Technol. **2013**, *47*, 1040

THERE ARE ALSO ENVIRONMENTAL AND SOCIAL COSTS



**REE tailings pond
near Baotou, China**



Gold extraction, NE Congo

NGM
Sept 2013

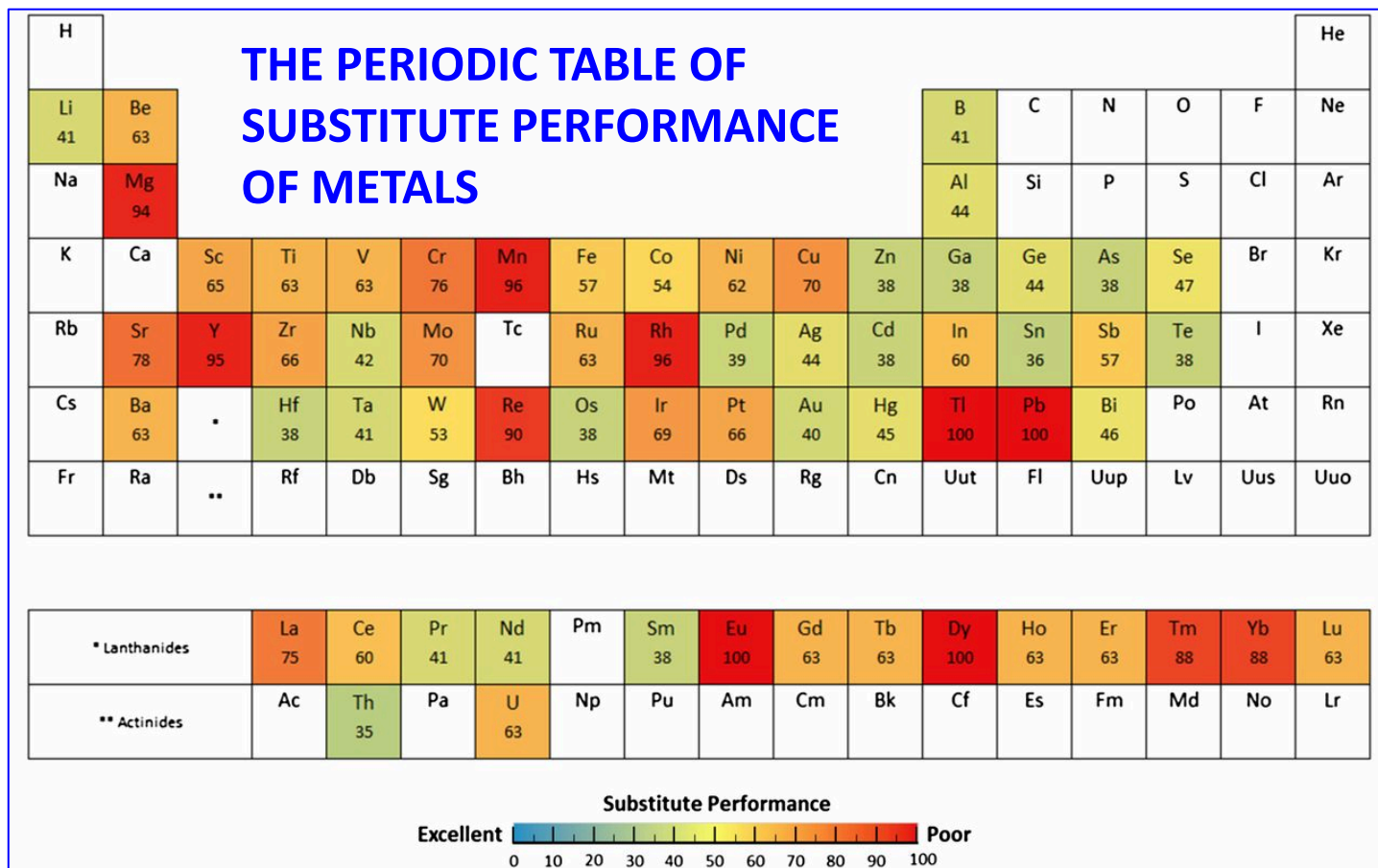


**Bingham Canyon Cu Mine
Utah, USA
(4 km wide, 1 km deep)**

TIME
15 Sept 2015



REPLACEMENT? NOT OFTEN POSSIBLE YET



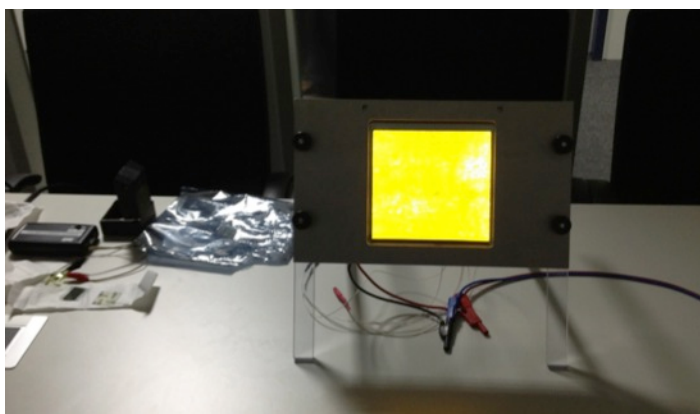
0 : exemplary substitutes exist for all major uses

100 : no substitute with adequate performance exists for any of the major uses

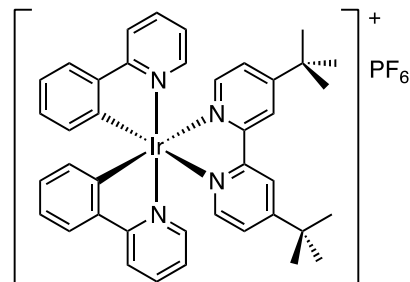
Proc. Natl. Acad. Sci. USA 2015, 112, 6295

AN EXAMPLE FROM OUR LAB AT CNR, Bologna

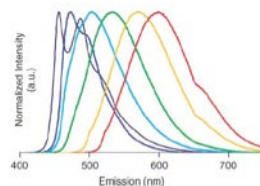
Application: flat lighting sources (OLEDs, LECs)



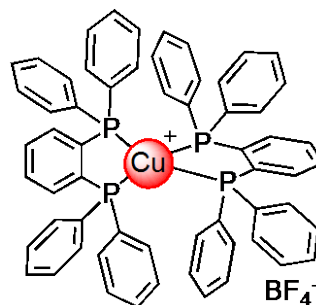
Standard materials:
Ir(III) metal complexes



- TUNABLE
- STABLE



Alternative materials:
Cu(I) metal complexes

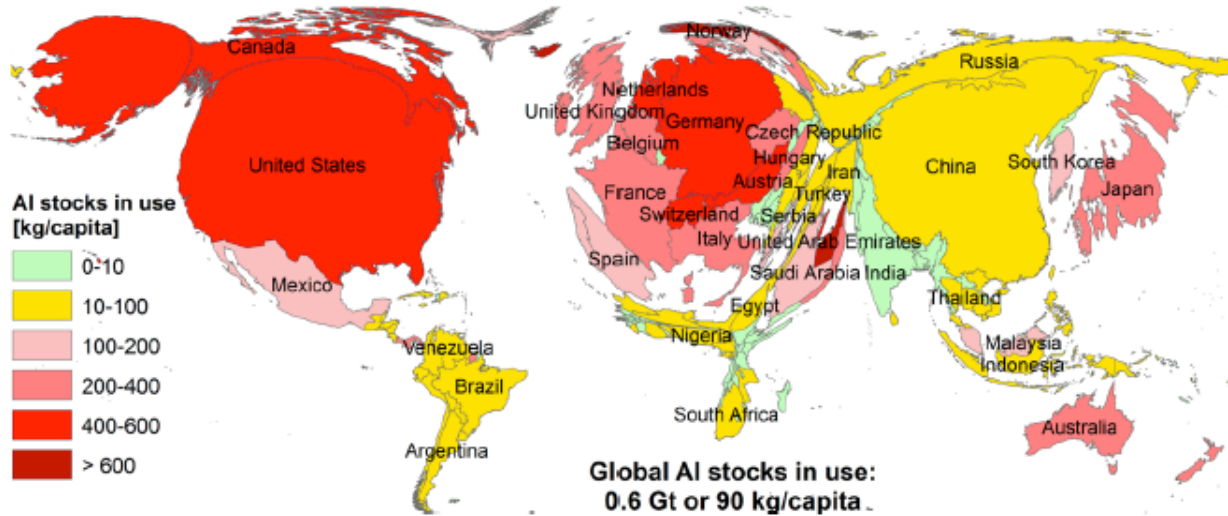


NOT COMPARABLY
TUNABLE AND STABLE

AND EUROPE?

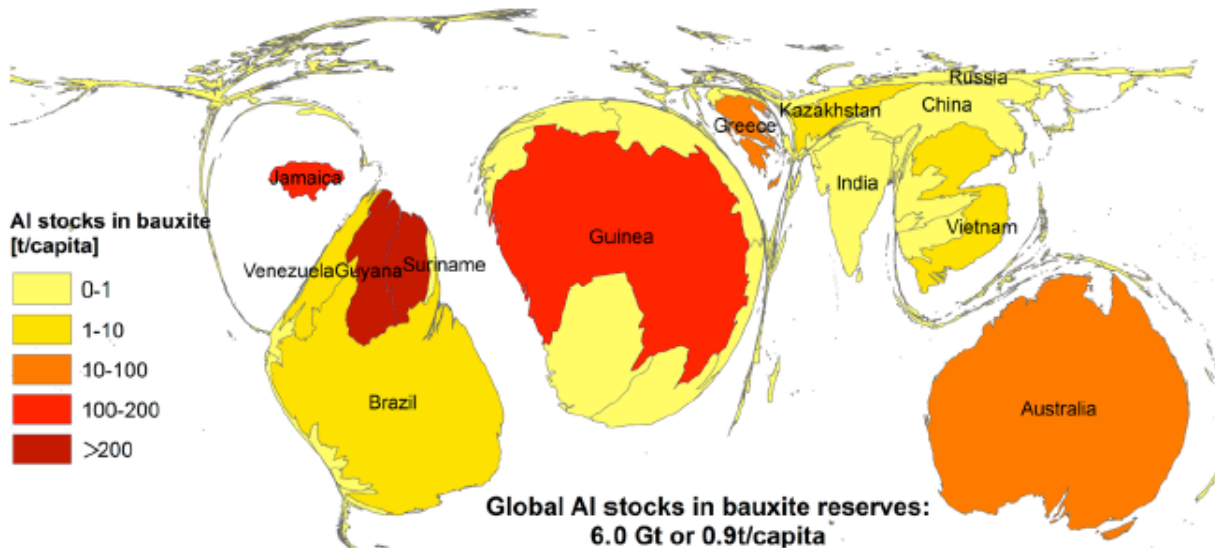


Large use, no stock: the case of ALUMINUM



IN USE

90 kg/capita

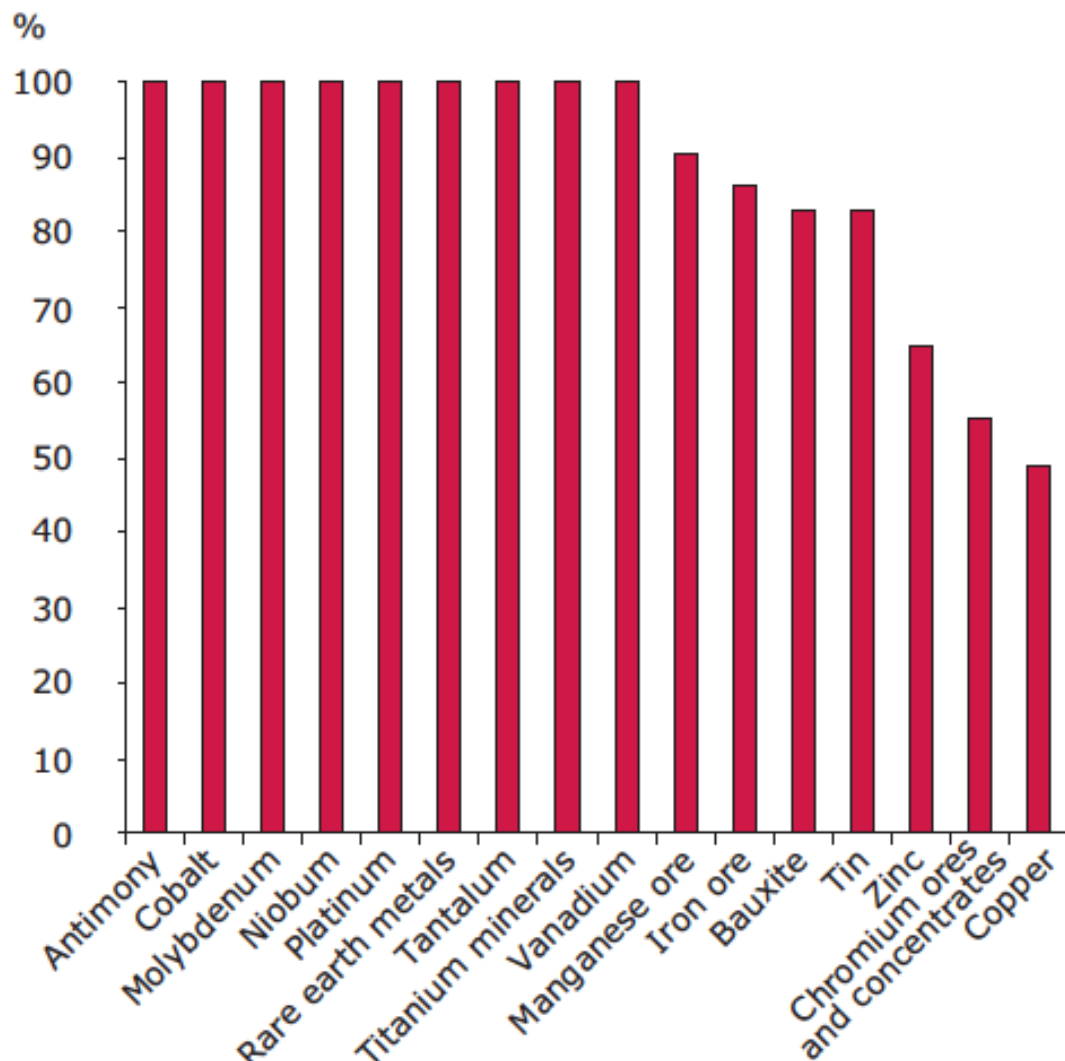


RESERVES
IN BAUXITE

900 kg/capita

Environ. Sci. Technol. 2013, 47, 4882

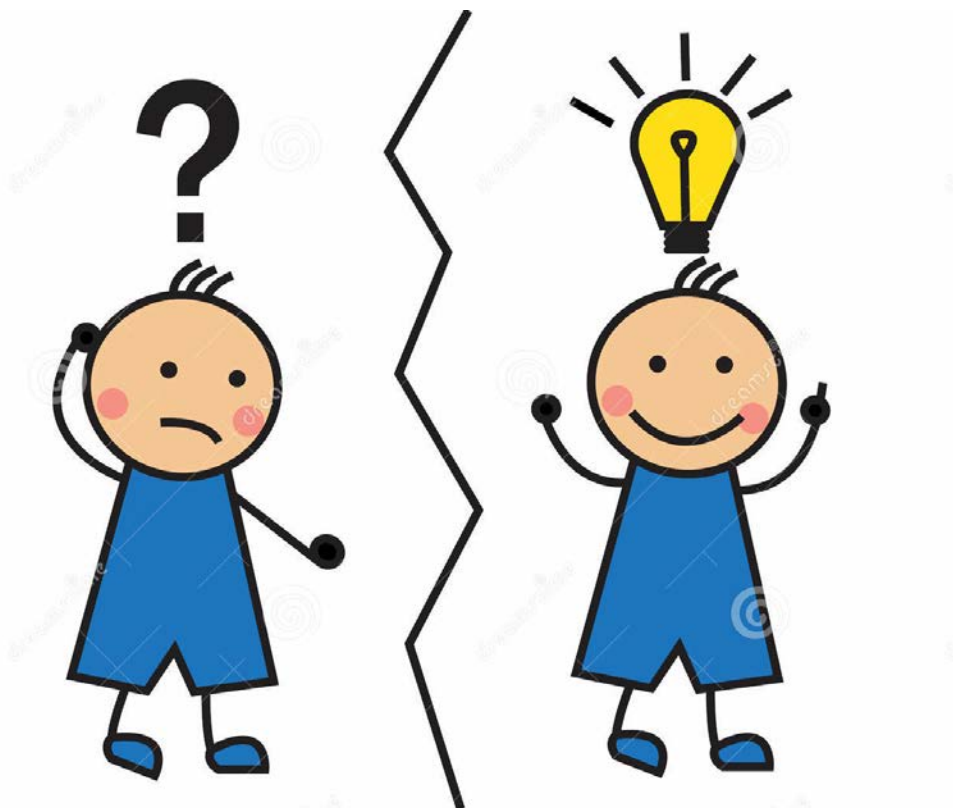
EU IMPORT OF METALS



**WE ALMOST TOTALLY
DEPEND ON IMPORTS**

Material Resources and Waste – Update 2012, EEA 2012

SOLUTIONS?

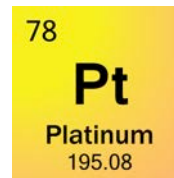


THE SCIENCE FICTION ONE: MINING ASTEROIDS

CONCENTRATION (ppb)

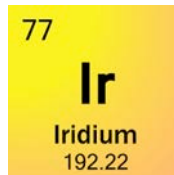
Earth

Asteroids



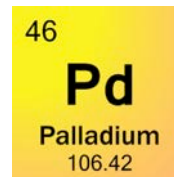
5

1400



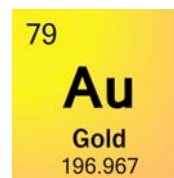
1

760



15

870



4

215

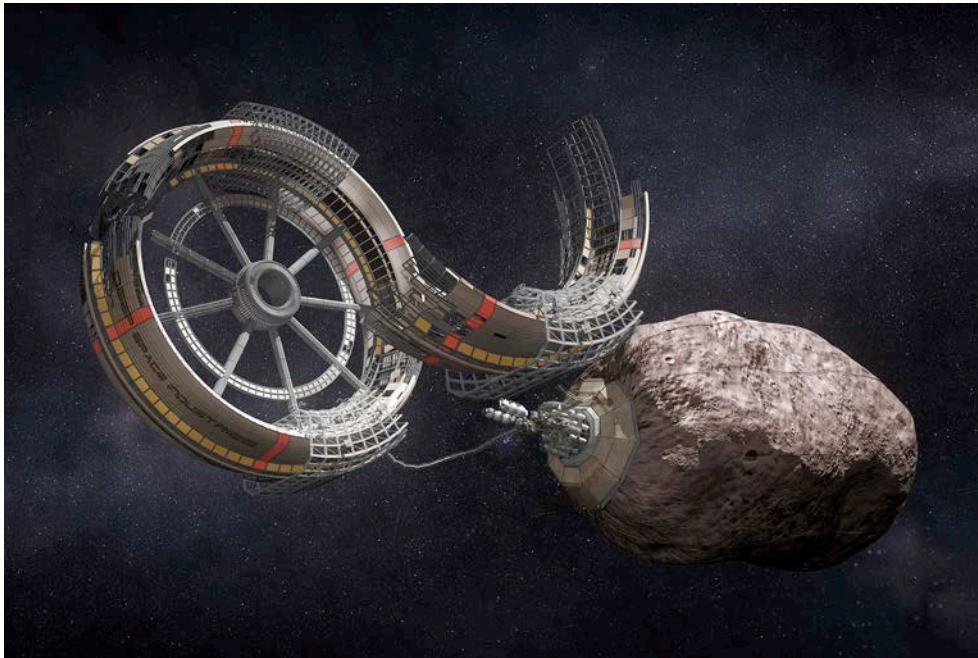


Photo Credit: National Geographic

This in NOT an option!

THE REAL ONE: RECYCLING

RATE OF RECYCLING OF METALS

1 H																	2 He						
3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg																	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	(117) (Uus)	118 Uuo						

Science
2012, 337, 690

* Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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

Present recycling rates are TOTALLY unacceptable

A (VERY) TENTATIVE ROADMAP

5-10 years

- Increase public awareness on Earth's material constraints
- Improve collecting policies
- Lobbying for more stringent regulations on material contents and recycling and ... information

RESEARCH

- Reduce the number of elements in, *e.g.*, electronic devices
- Reduce mixing of elements to enhance traceability
- Enable standardized disassembly protocols

10-30 years

- Waste collection > 90% worldwide
- A reliable world inventory of recoverable mineral resources
- International agreements on fair use and exploitation of mineral resources to prevent resource wars

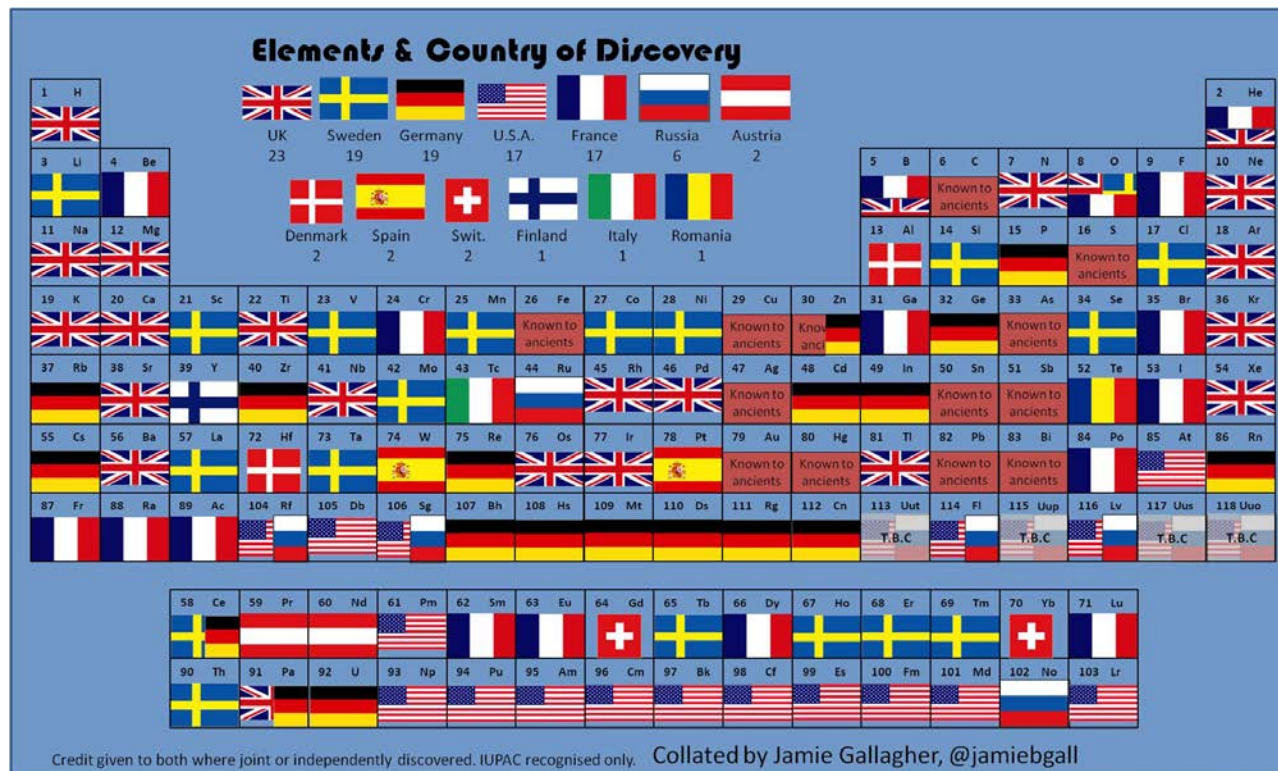
RESEARCH

- Find adequate replacements for any applications
- Reduce energy consumption of recycling by at least 50%
- Target a standard > 80% recycling rate

SUMMARY

- There is only one relevant and utterly abundant (extraterrestrial) resource for planet Earth: **solar radiation**
- On the contrary, all kinds of materials must be **obtained from planet Earth**, a sort of spaceship with **limited resources** in its hold
- Criticality of elements is dictated by (1) **natural availability**, (2) **environmental implications**, (3) **vulnerability to supply risk**
- We need to develop **recycling protocols** at all levels and for any products, in order to secure the **availability of chemical elements** and hence the **quality of life** of human beings on the long term
- WARNING. The 2nd Principle works against us and, sometimes, recycling may become **downcycling** with materials being used for lower-grade applications

A FINAL CONSIDERATION



**85% of chemical elements
were discovered in Europe, so ...**