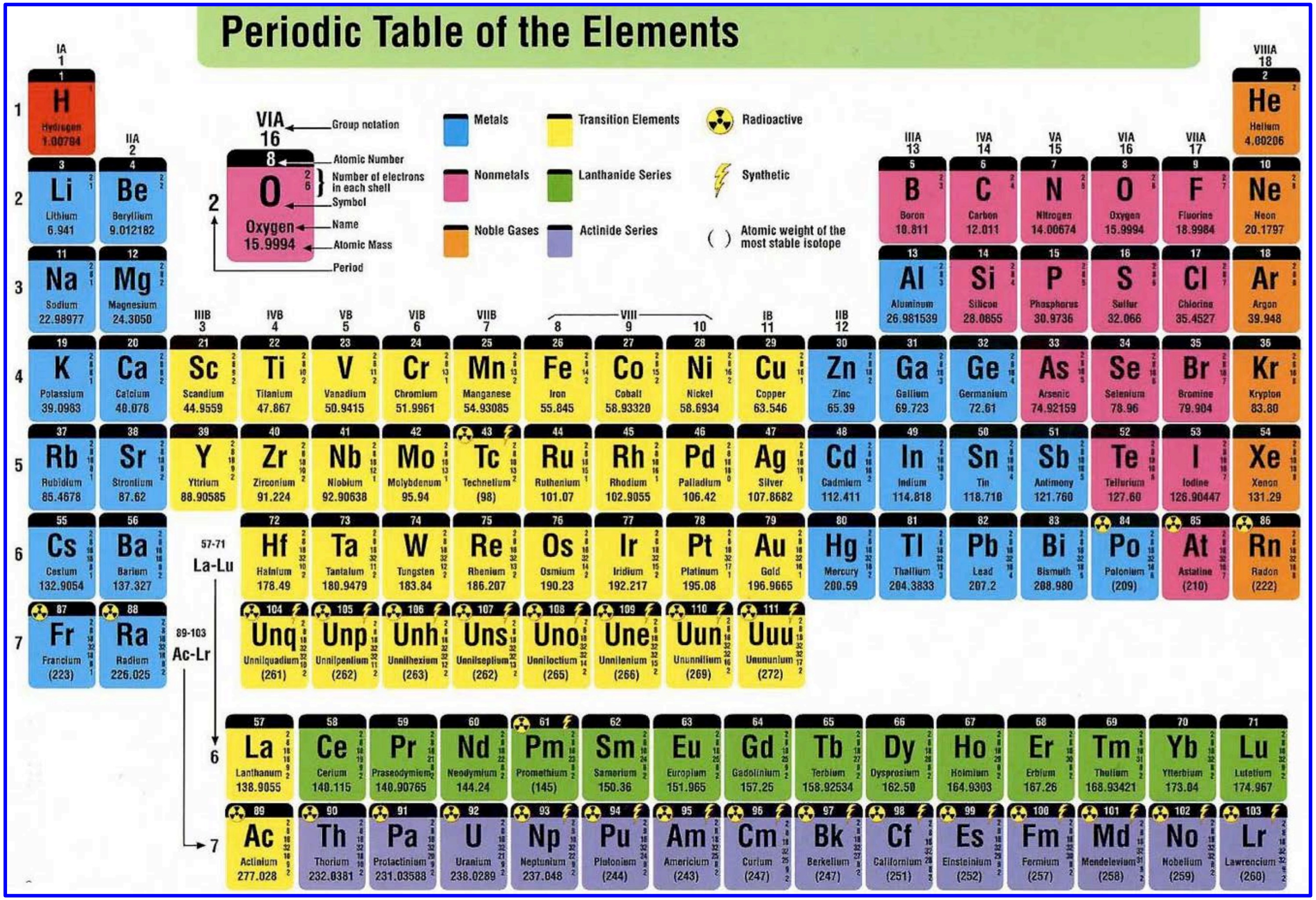
HUNTING THE ELEMENTS OF THE PERIODIC TABLE ON SPACESHIP EARTH

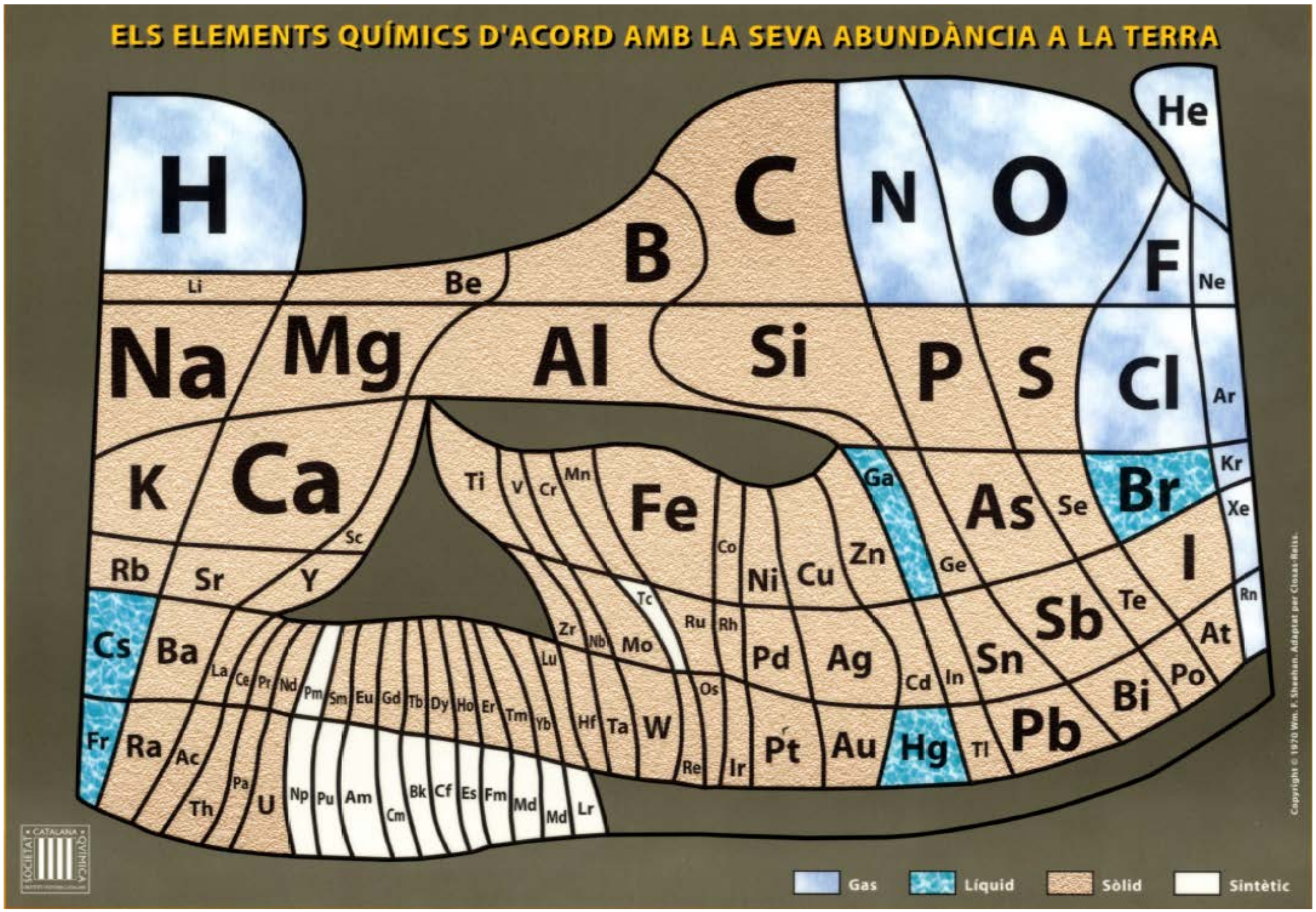
Nicola Armaroli
Istituto per la Sintesi Organica e la Fotoreattività
Consiglio Nazionale delle Ricerche, Bologna
nicola.armaroli@cnr.it

EuCheMS
Brussels, September 22, 2015

PERIODIC TABLE
– The ordinary picture –



PERIODIC TABLE
– The quantitative picture –

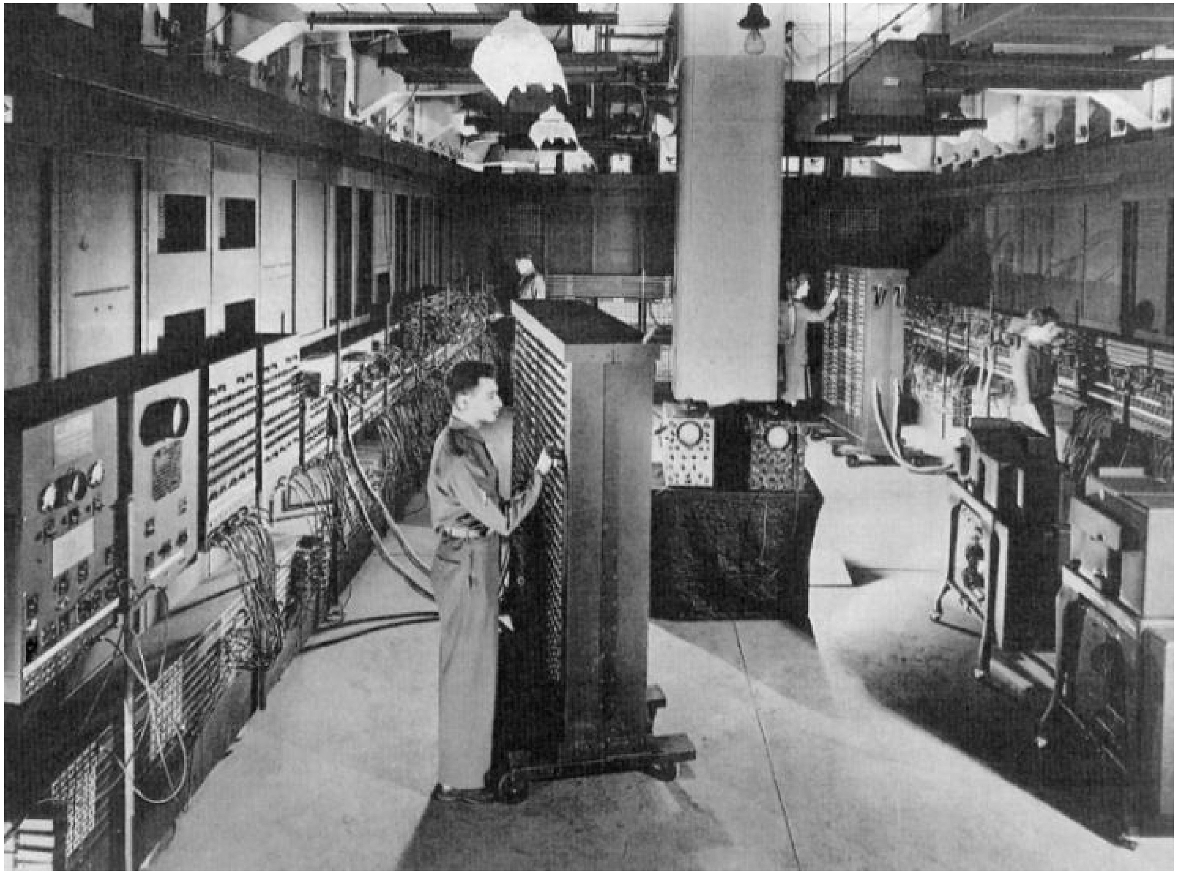


Nicola Armaroli, CNR, Italy – *Protecting Endangered Elements*, EuCheMS , Brussels, Sept. 22, 2015

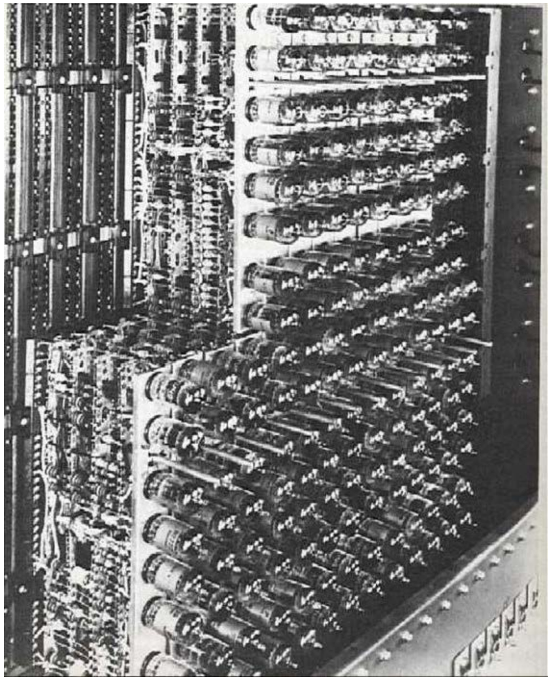
DEMATERIALISATION

ENIAC

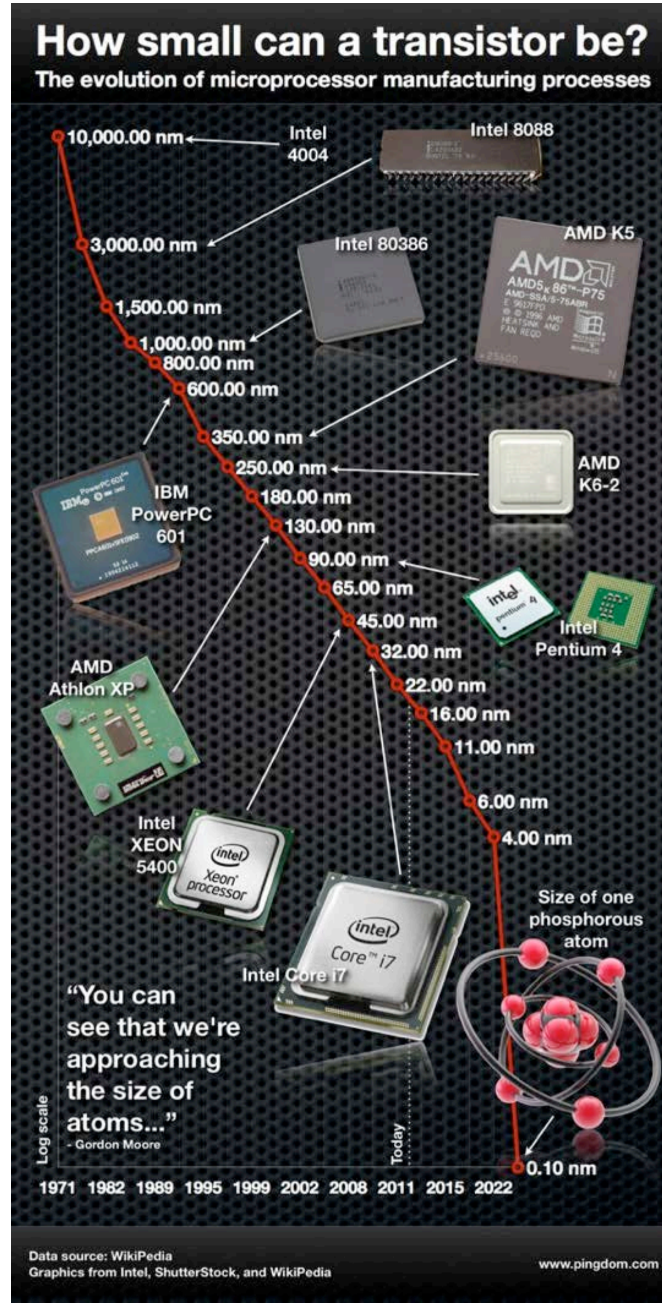
the first electronic computer (1944)



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



THIS COMPUTER



Weigth: 1.5 kg

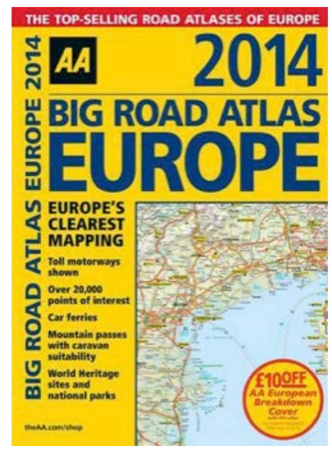
Consumption: 30 W

1.3 billions of transistors

Average dimension: 22 nm

THE CHAMPION OF DEMATERIALIZATION

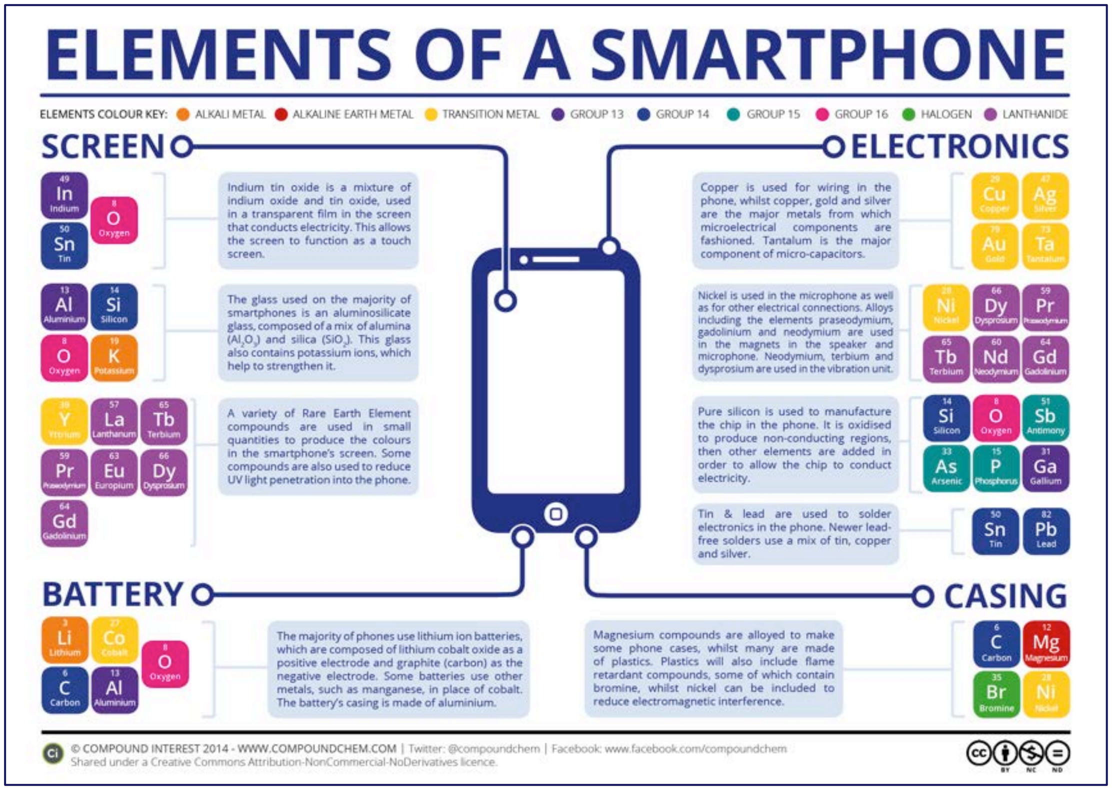
129 grams



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

2015

Over 40 elements in a mobile phone



Source: http://www.compoundchem.com

1990

Less than 20 elements in an entire house

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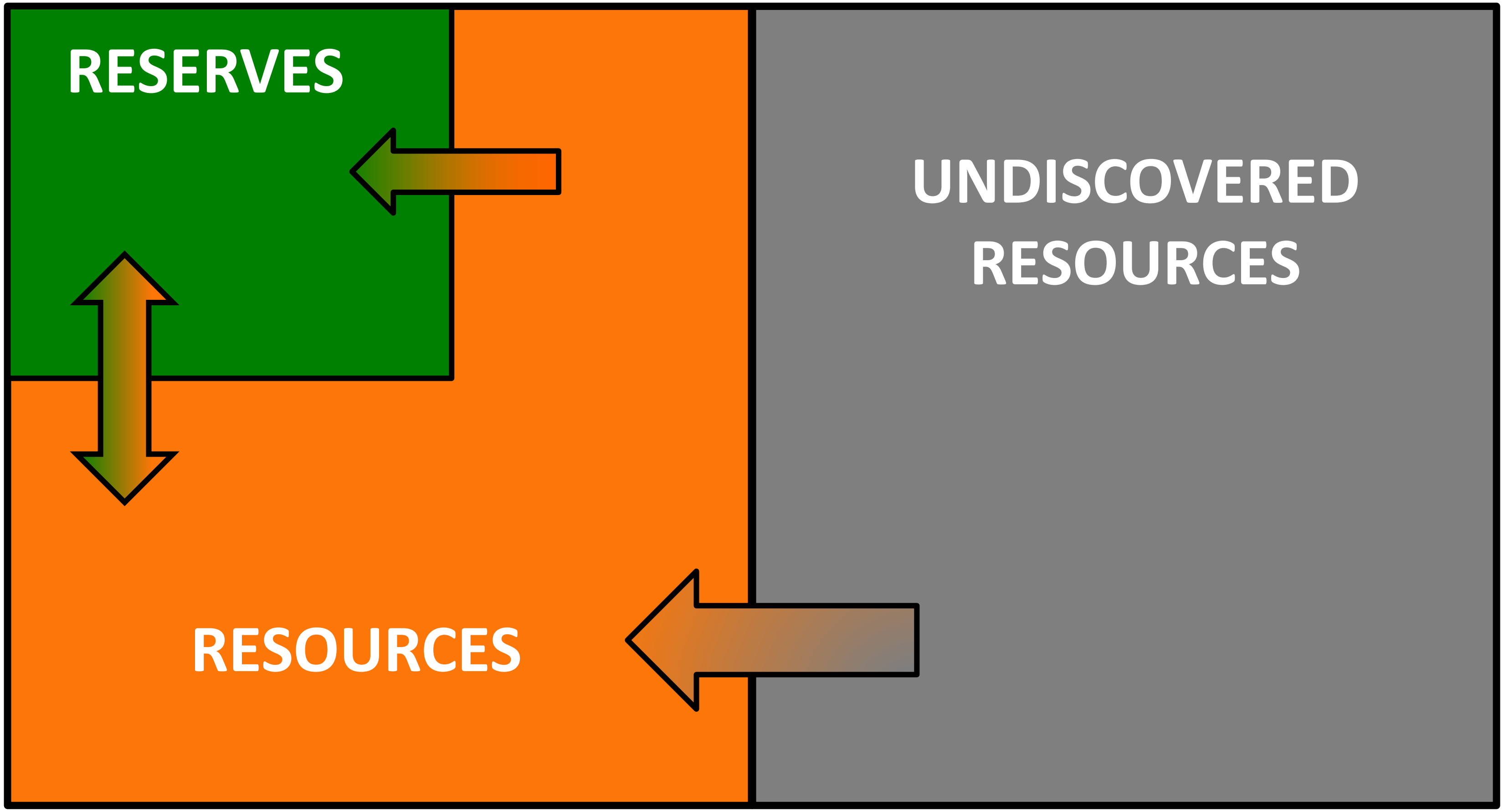
DEMATERIALISATION

MATERIAL
<u>INTENSIFICATION</u>

OUR "MINE": A TINY SPACESHIP EARTH

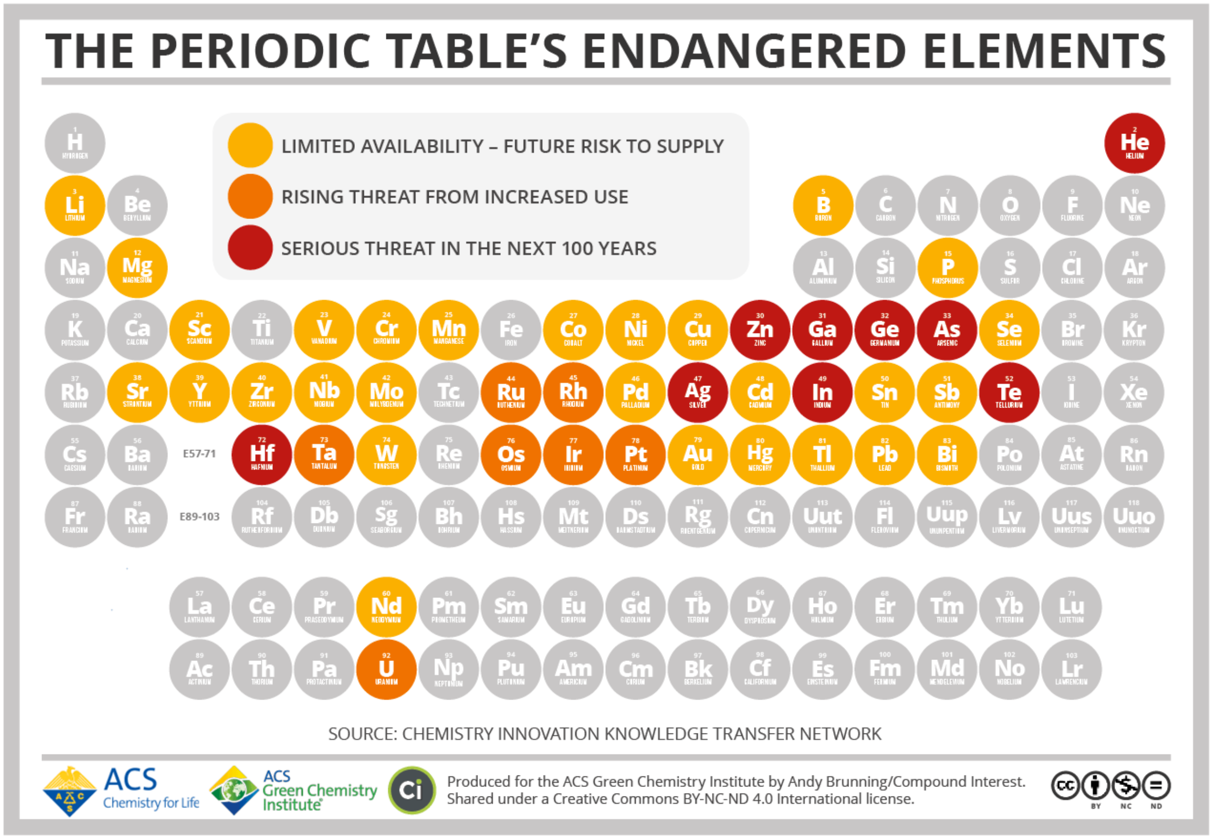
We can dig down to about <u>5 km</u>

MINERAL "RESOURCES" AND "RESERVES"



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

ENDANGERED ELEMENTS: SELECTED EXAMPLES



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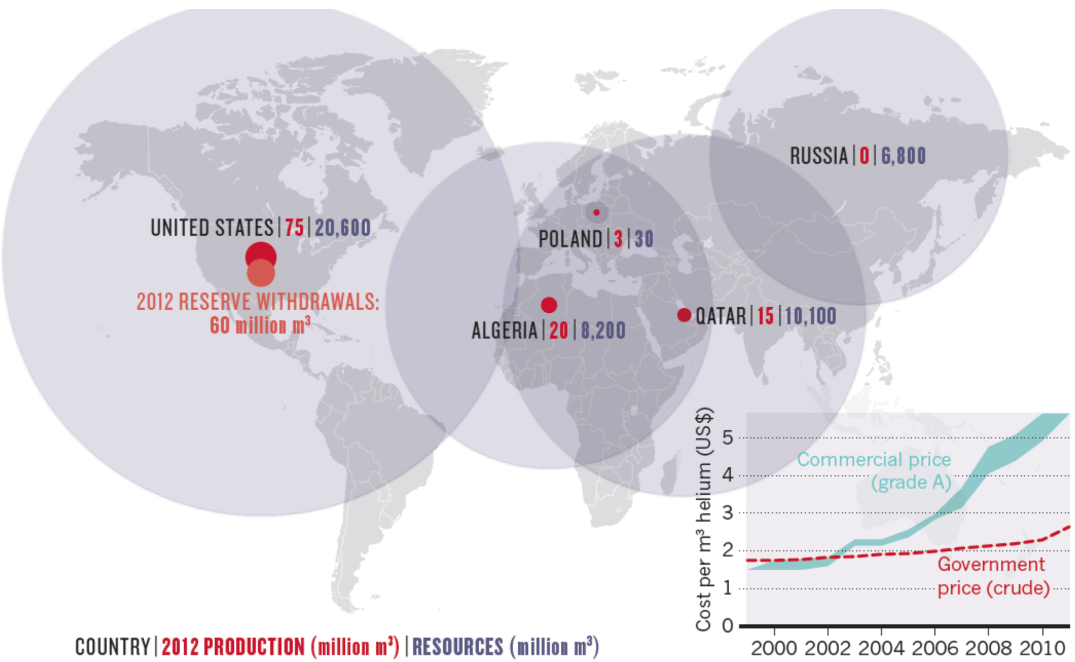
HELIUM

helium
2
He
4.0026

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

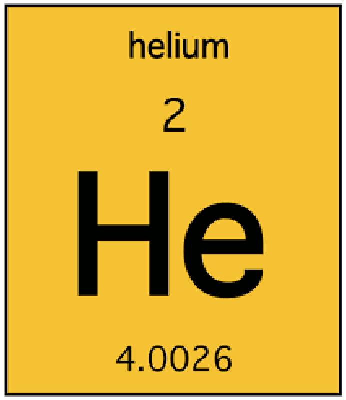
Main source: natural gas wells (from nuclear decay)



Nature **2013**, *497*, 168

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

HELIUM: Absolutely unique physical properties

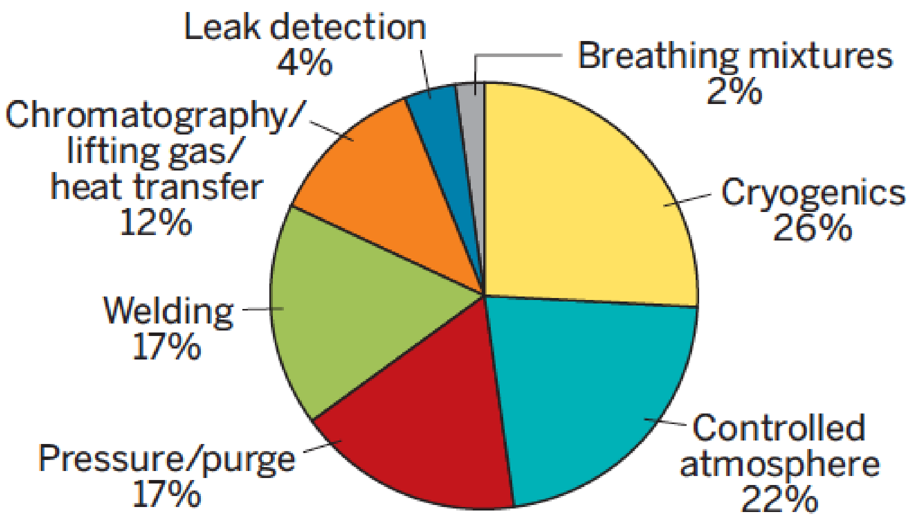


Boiling point: -268,93 ° C (4.22 K)

Melting point: -272,20 ° 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*

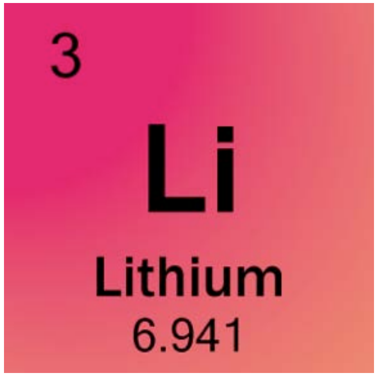
LITHIUM

3
Li
Lithium
6.941

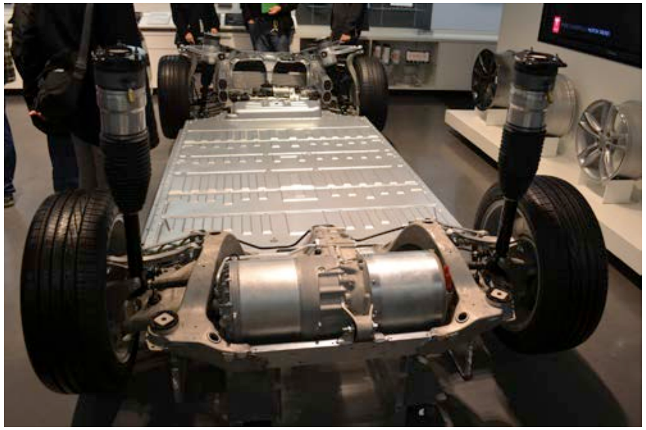
METAL – very unstable in air and water.
Major producers: Australia, Chile and China.
Estimated world reserves: 13.5 Mton

The largest resource in the world:
Salar de Uyuni, Bolivia
$10,000\ km^2$

LITHIUM: demand projected to explode



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



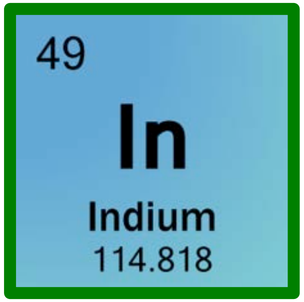
Cars sold per year worldwide: 70 millions

If electric : ≈ 700 000 ton of Li required

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

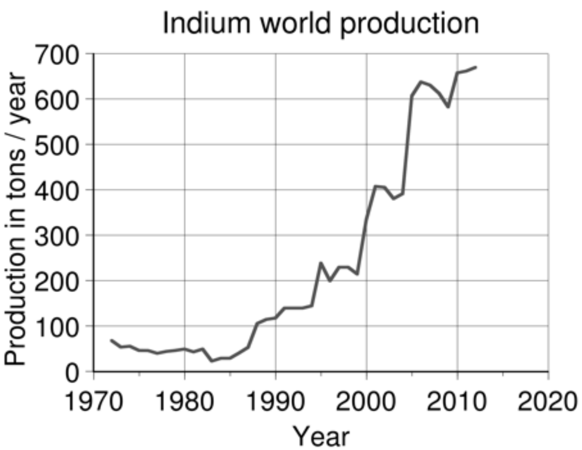
Lithium is also needed for portable devices, ceramics, lubricants, alloys and … Tritium (nuclear fusion).
RECYCLING WILL BE CRUCIAL (not difficult)

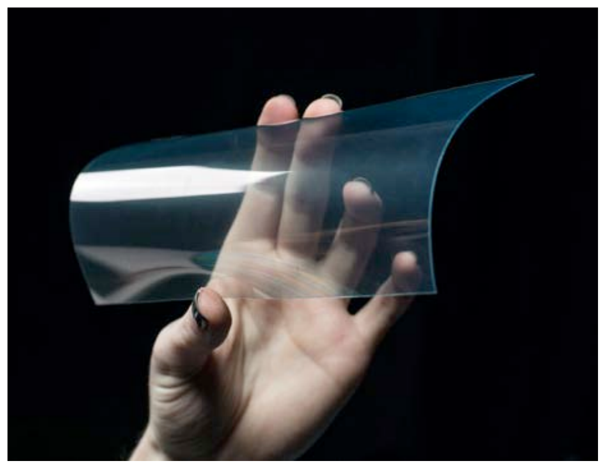
INDIUM

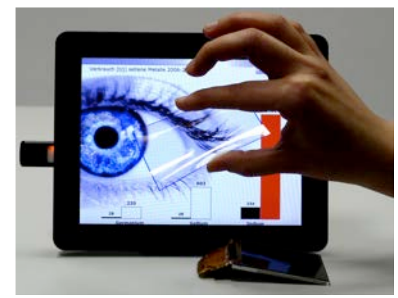


METAL – soft and stable in air and water. Major producers: China, South Korea and Japan. Estimated reserves: unknown (USGS, 2015)

Relatively useless until 20 years ago, then …

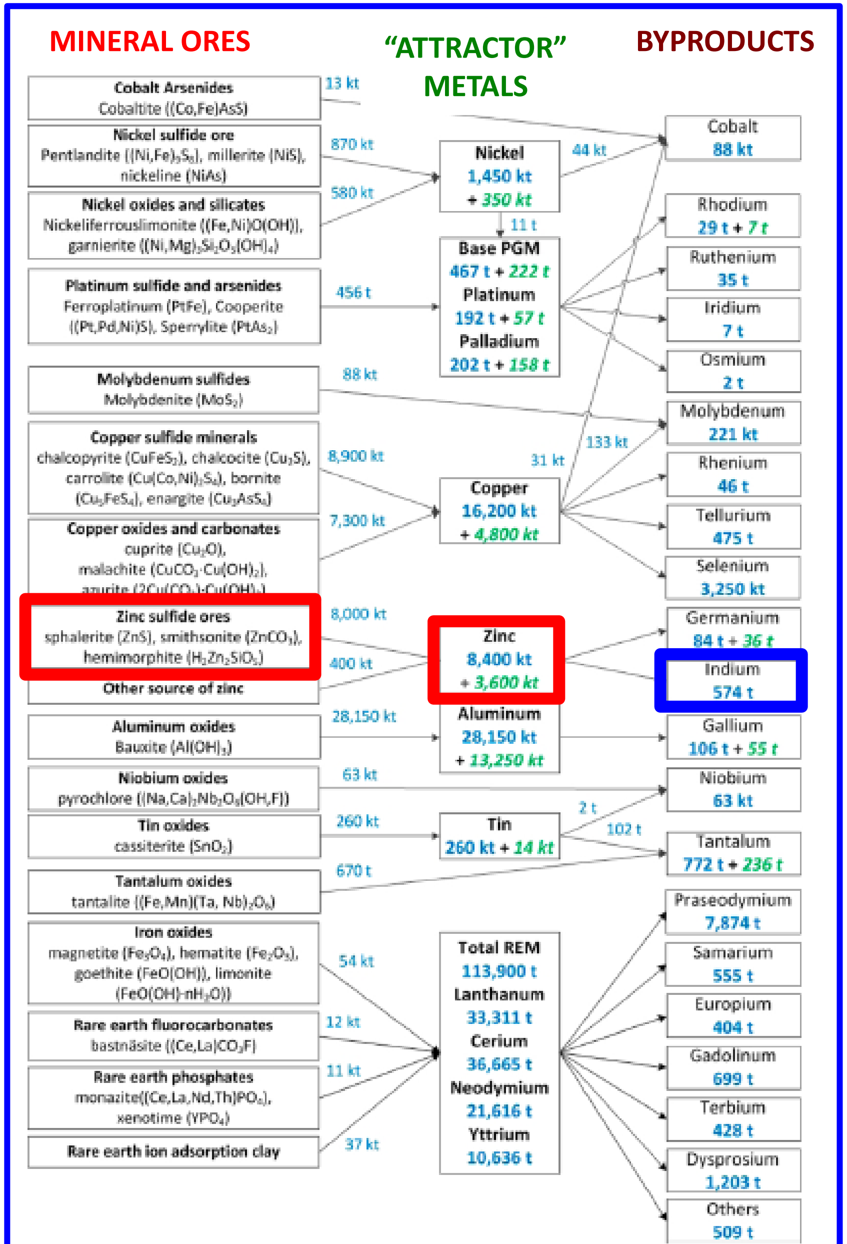






Indium Tin Oxide (ITO)

Transparent, conductor, binds strongly to glass



Environ. Sci. Technol. **2013**, *47*, 2939

INDIUM IS NOT OBTAINED DIRECTLY

ATTRACTOR METALS

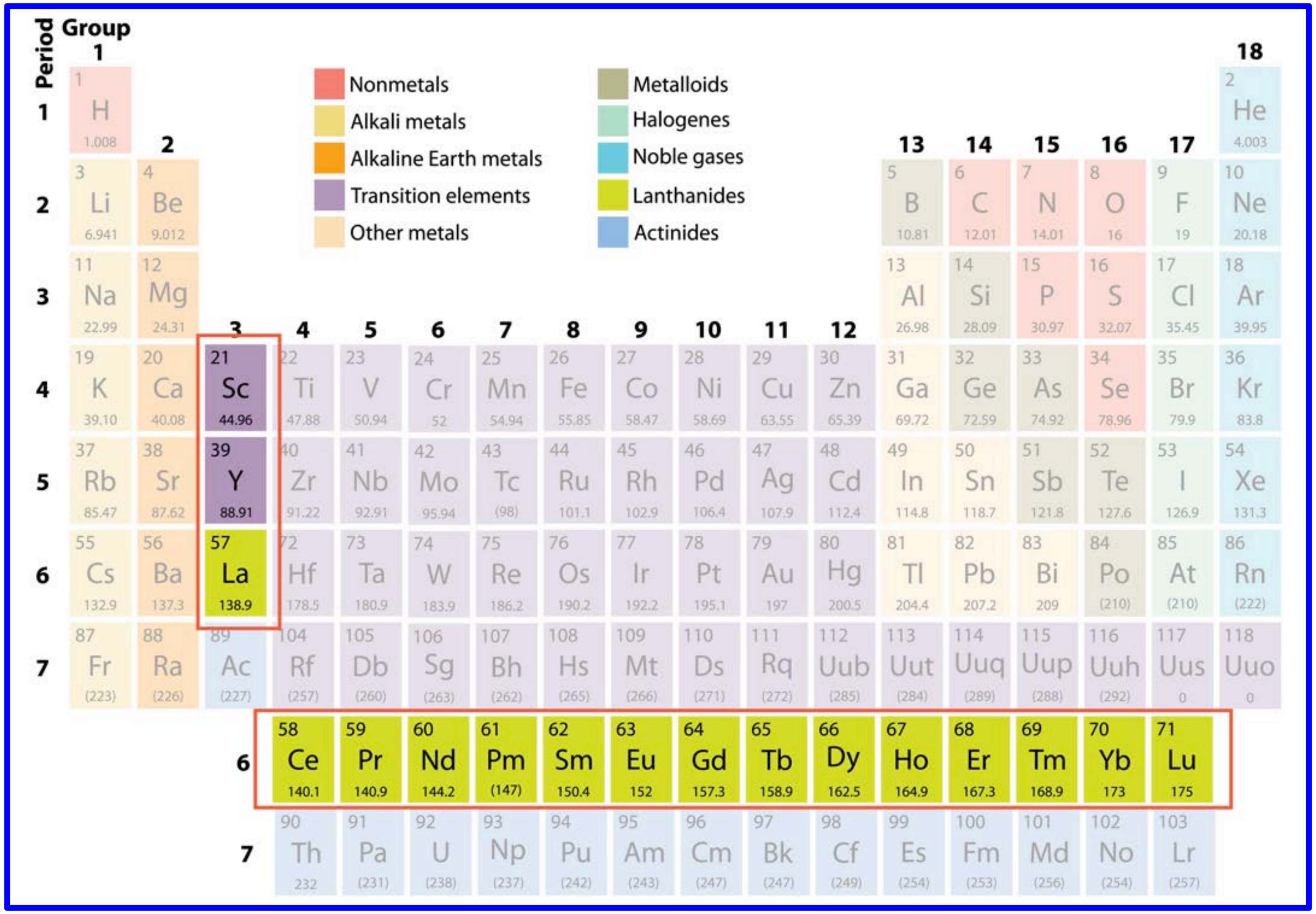
(Pt, Pd, Cu, Zn, Al, Sn, La, Ce, Nd, Y)

"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

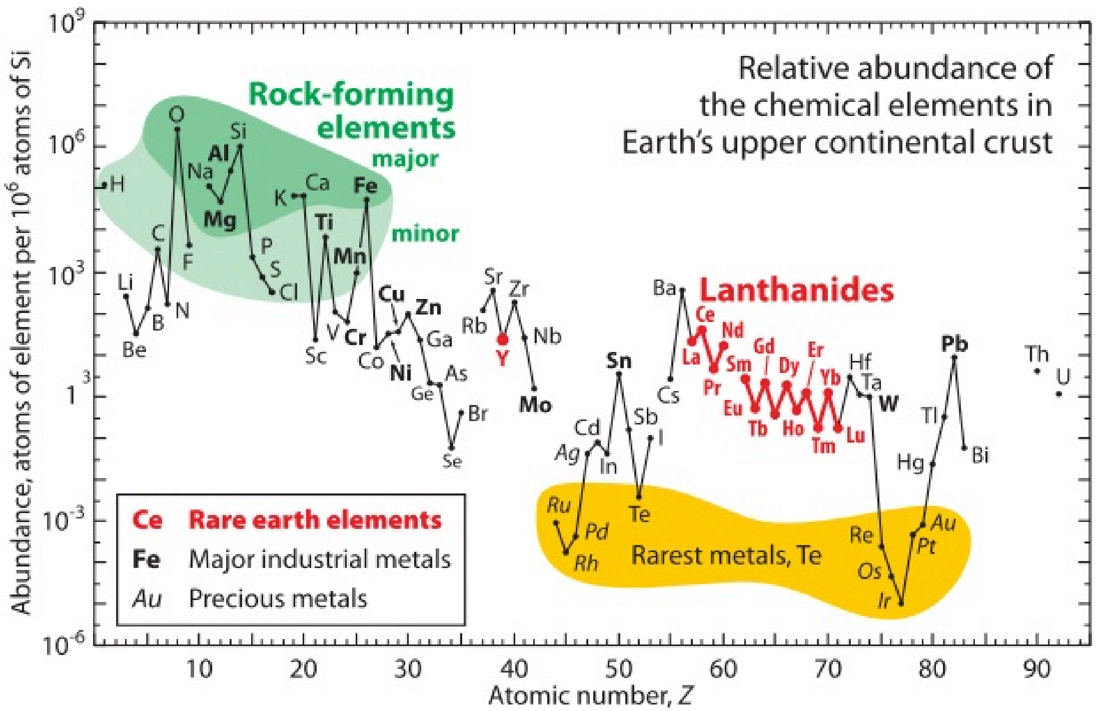
RARE EARTH ELEMENTS (REE)



Unique
MAGNETIC
PHOSPHORESCENT
OPTICAL
CATALYTIC
properties

14 "LANTHANIDES" (no Pm) + Sc and Y

RELATIVE CONCENTRATION OF ELEMENTS (upper continental crust)

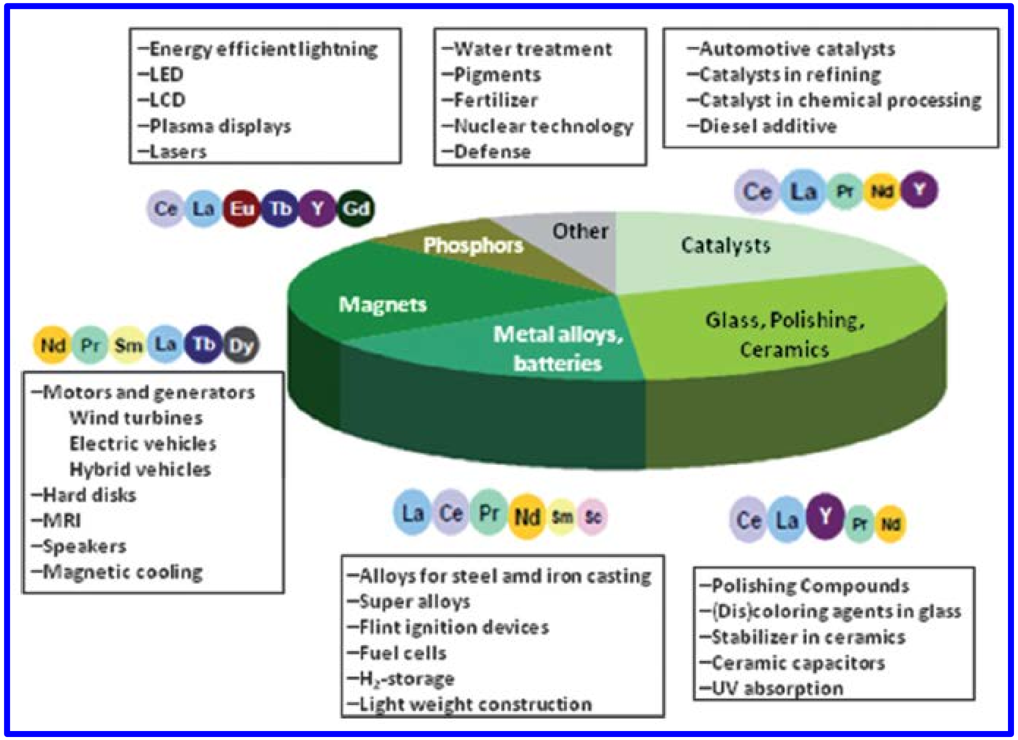


REE ARE NOT SO RARE BUT ARE RARELY CONCENTRATED ENOUGH TO SUPPORT ECONOMICALLY CONVENIENT RECOVERY

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

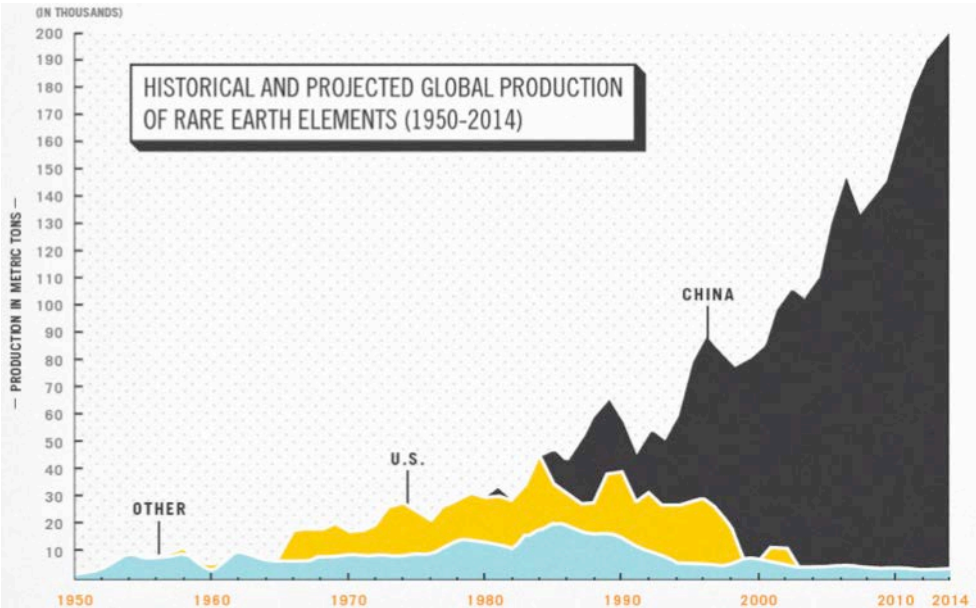


ChemSusChem **2013**, *6*, 2045

REE IN SMARTPHONES

http://www.rareelementresources.com

REE: THE CHINESE SUPPLY MONOPOLY



No good news from U.S.

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

BUSINESS

THE STRUGGLE TO MINE RARE EARTHS

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

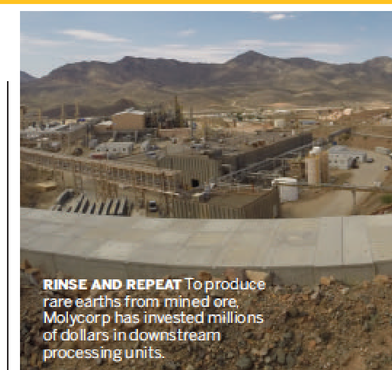
MELODY M. BOMGARDNER, C&EN WEST COAST NEWS BUREAU

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 creditors 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.

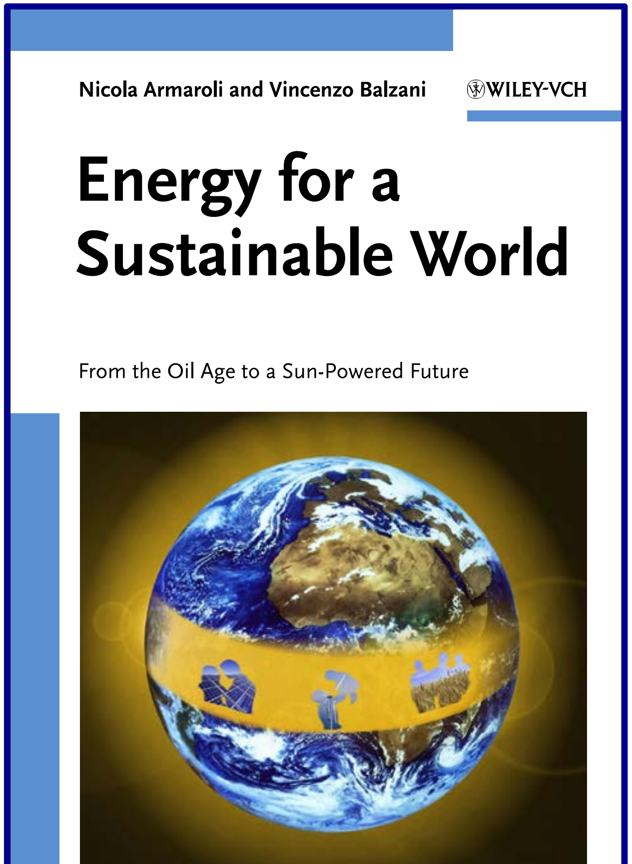
China's near-monopoly gained widespread attention in 2010 when the country lowered export quotas for rare earths, causing prices to skyrocket. Starting in 2012, however, prices began to decline. In May, China did away with the quotas following a ruling from the World Trade Organization.

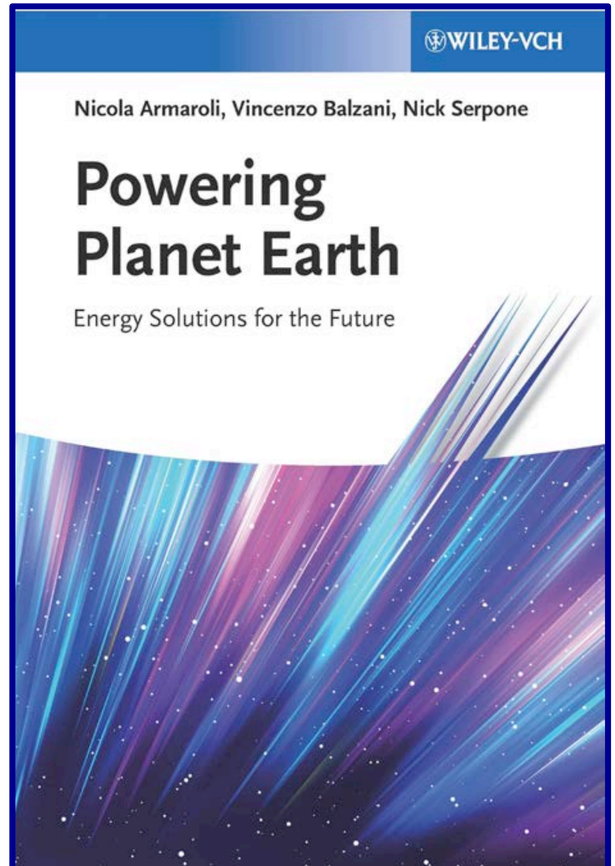


RINSE AND REPEAT To produce rare earths from mined ore, Molycorp has invested millions of dollars in downstream processing units.

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.

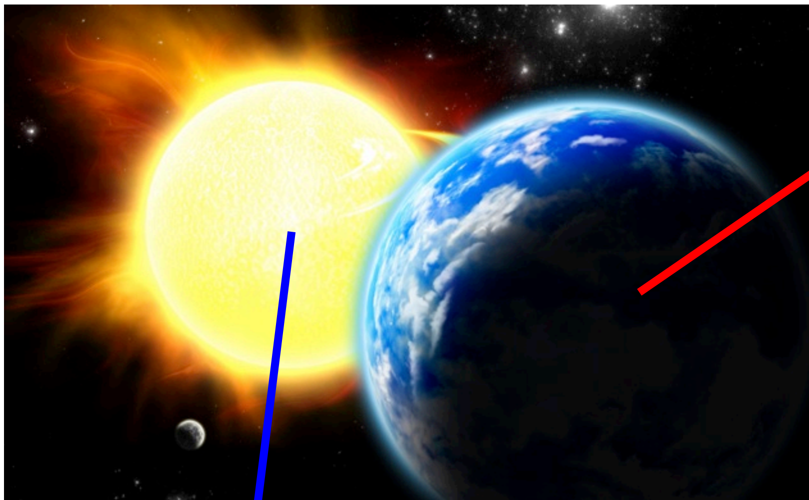
ENDANGERED ELEMENTS AND THE TRANSITION TO A SUN-POWERED WORLD





FOR USING SOLAR ENERGY WE NEED PHOTONS ...

... AND ATOMS (*i.e.*, CHEMICAL ELEMENTS)



We need <u>CONVERTERS</u> of solar energy, made of "terrestrial" materials, which are available in limited supply

Photons are an overabundant "extraterrestrial" input amounting to <u>THOUSANDS</u> of times our needs

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,

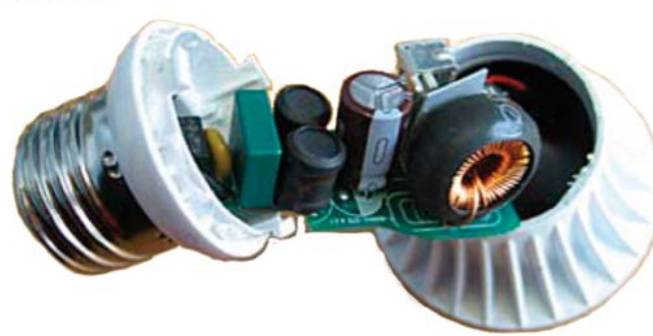
Europium, Terbium,
Yttrium, Cerium

LIGHTING EFFICIENCY COMES AT A PRICE

	INC.	LED	CFL
Power	60 W	10 W	13 W
Lifetime	1200 h	25000 h	10000 h
Metal	1 g	170 g	10 g

(a) CFL Bulb Driver

(b) LED Bulb Driver



METAL CONTENT

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

THERE ARE ALSO ENVIRONMENTAL AND SOCIAL COSTS

REE tailings pond
near Baotou, China

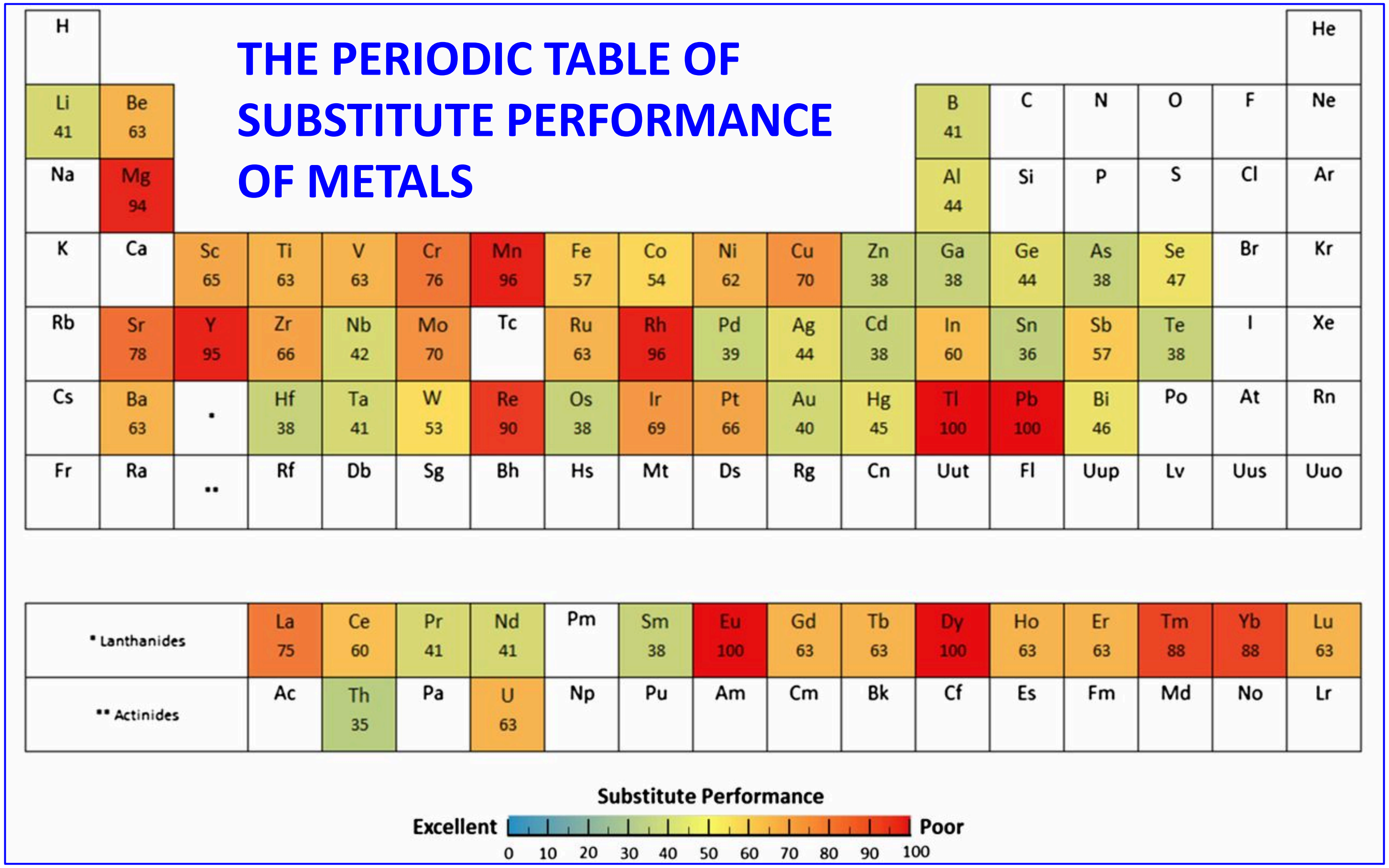
Gold extraction, NE Congo

NGM
Sept 2013

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

TIME
15 Sept 2015

REPLACEMENT? NOT OFTEN POSSIBLE YET



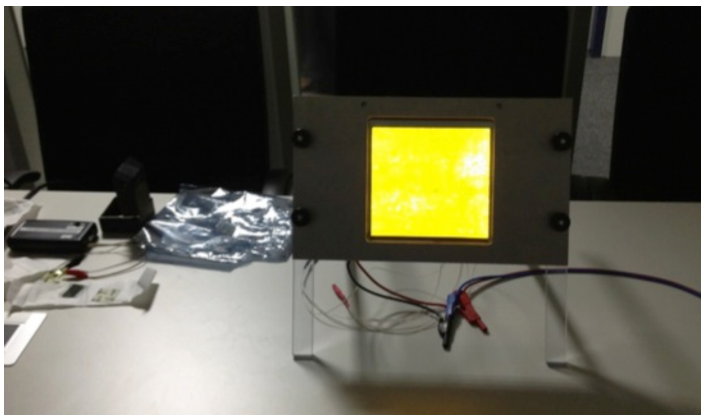
0 : exemplary substitutes exist for all major uses

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

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

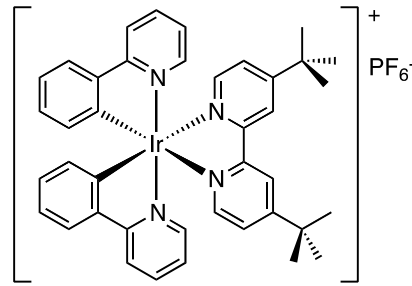
AN EXAMPLE FROM OUR LAB AT CNR, Bologna

Application: flat lighting sources (OLEDs, LECs)

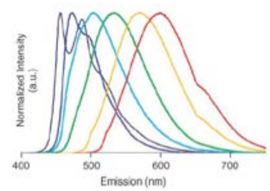


cello
RESEARCH FOR LOW COST
FLEXIBLE LIGHTING SOLUTIONS

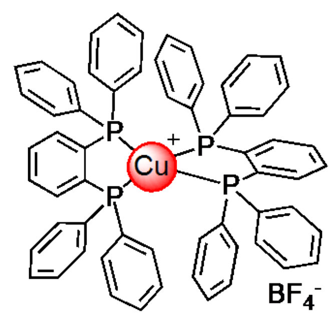
Standard materials: Ir(III) metal complexes



- TUNABLE
- STABLE



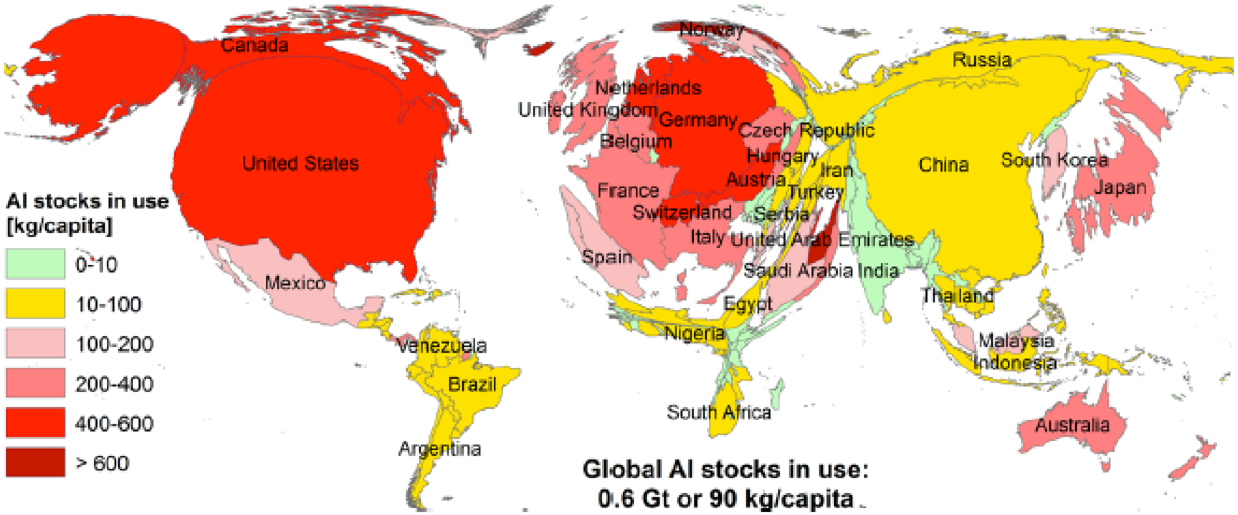
Alternative materials: Cu(I) metal complexes



NOT COMPARABLY TUNABLE AND STABLE

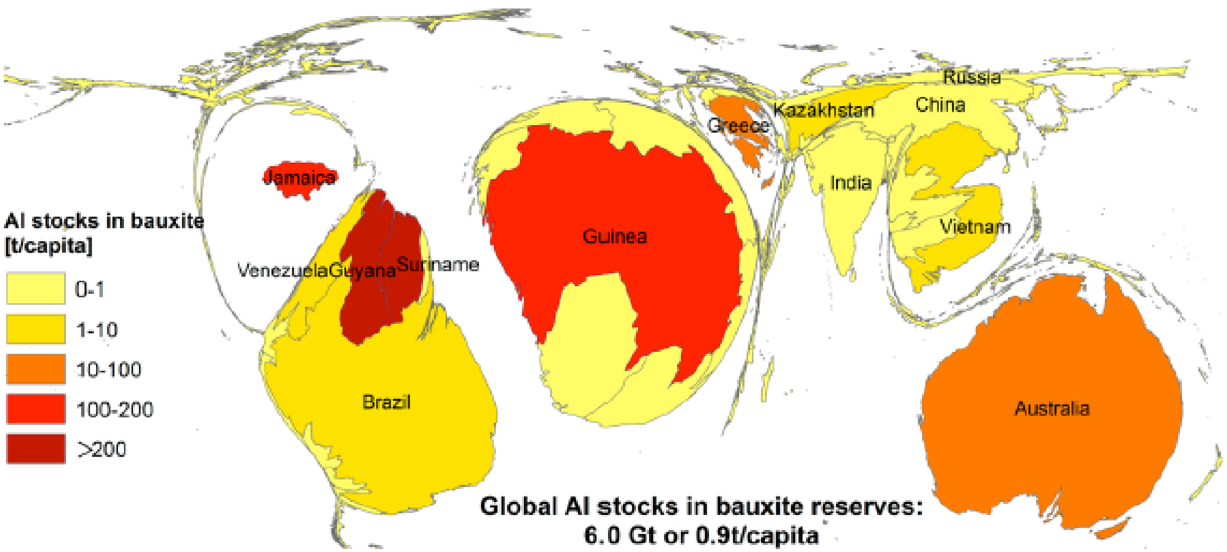
AND EUROPE?

Large use, no stock: the case of ALUMINUM



IN USE

90 kg/capita

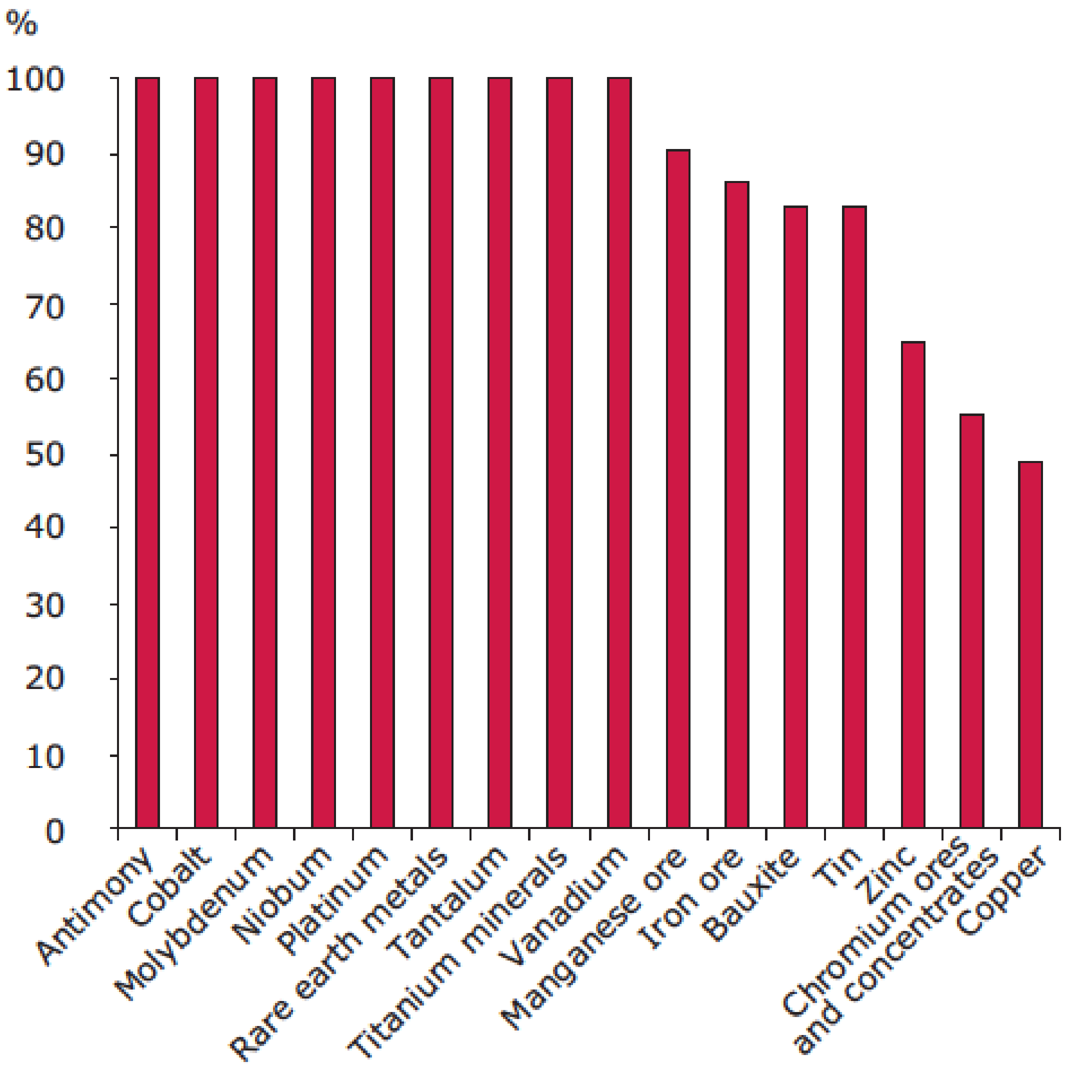


RESERVES
IN BAUXITE

900 kg/capita

Environ. Sci. Technol. **2013**, *47*, 4882

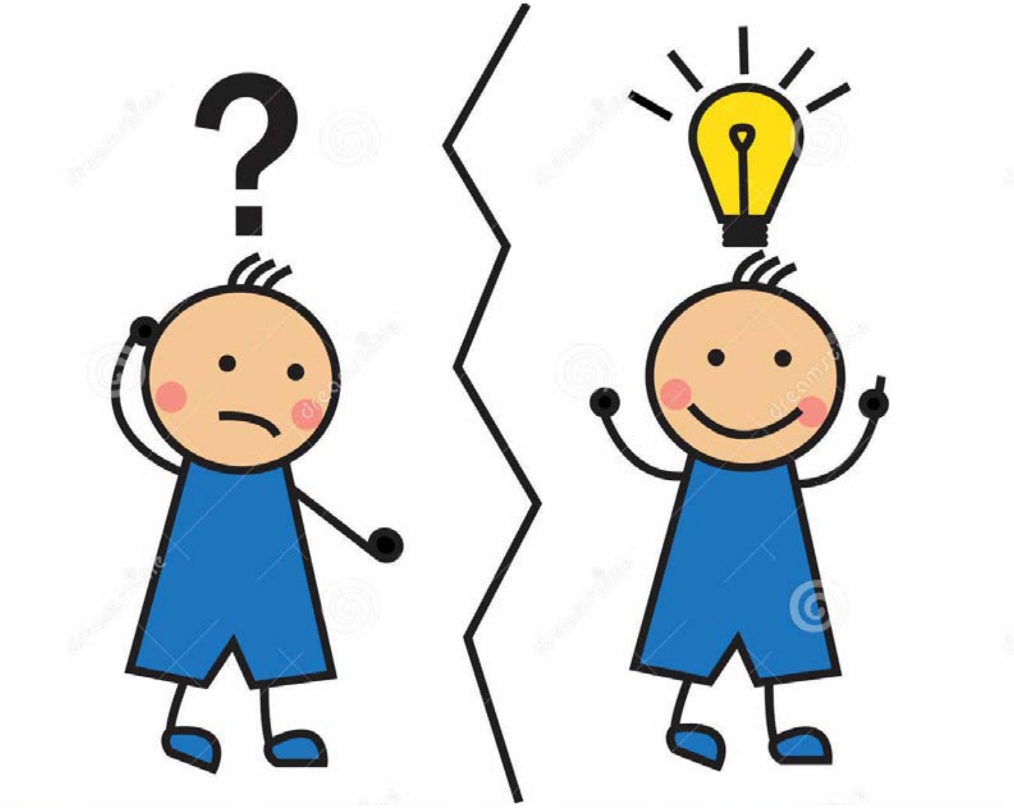
EU IMPORT OF METALS



WE ALMOST TOTALLY DEPEND ON IMPORTS

Material Resources and Waste – Update 2012, EEA **2012**

SOLUTIONS?



THE SCIENCE FICTION ONE: MINING ASTEROIDS

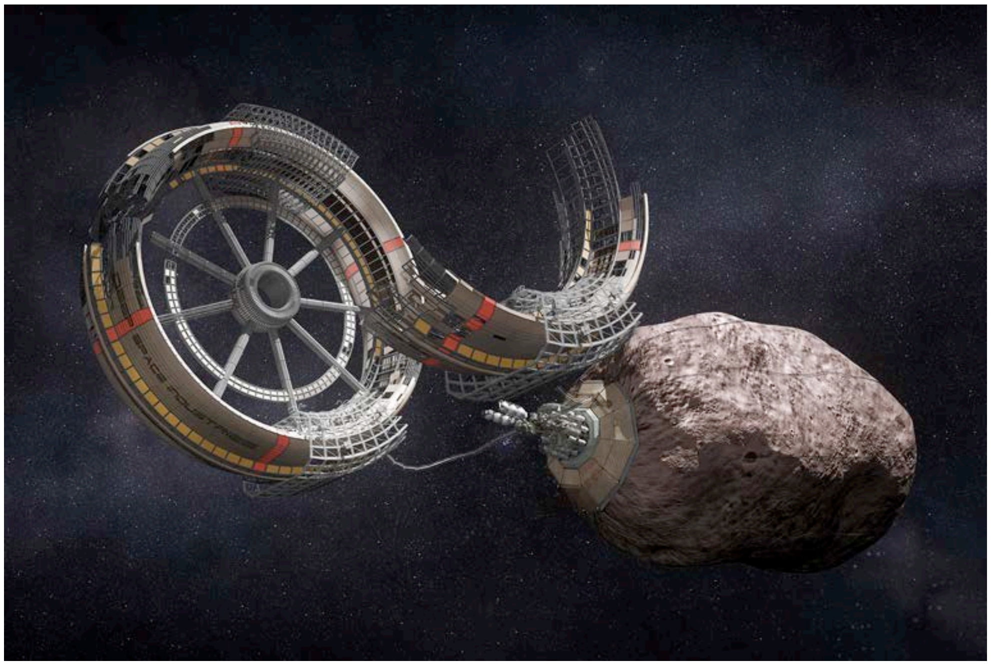


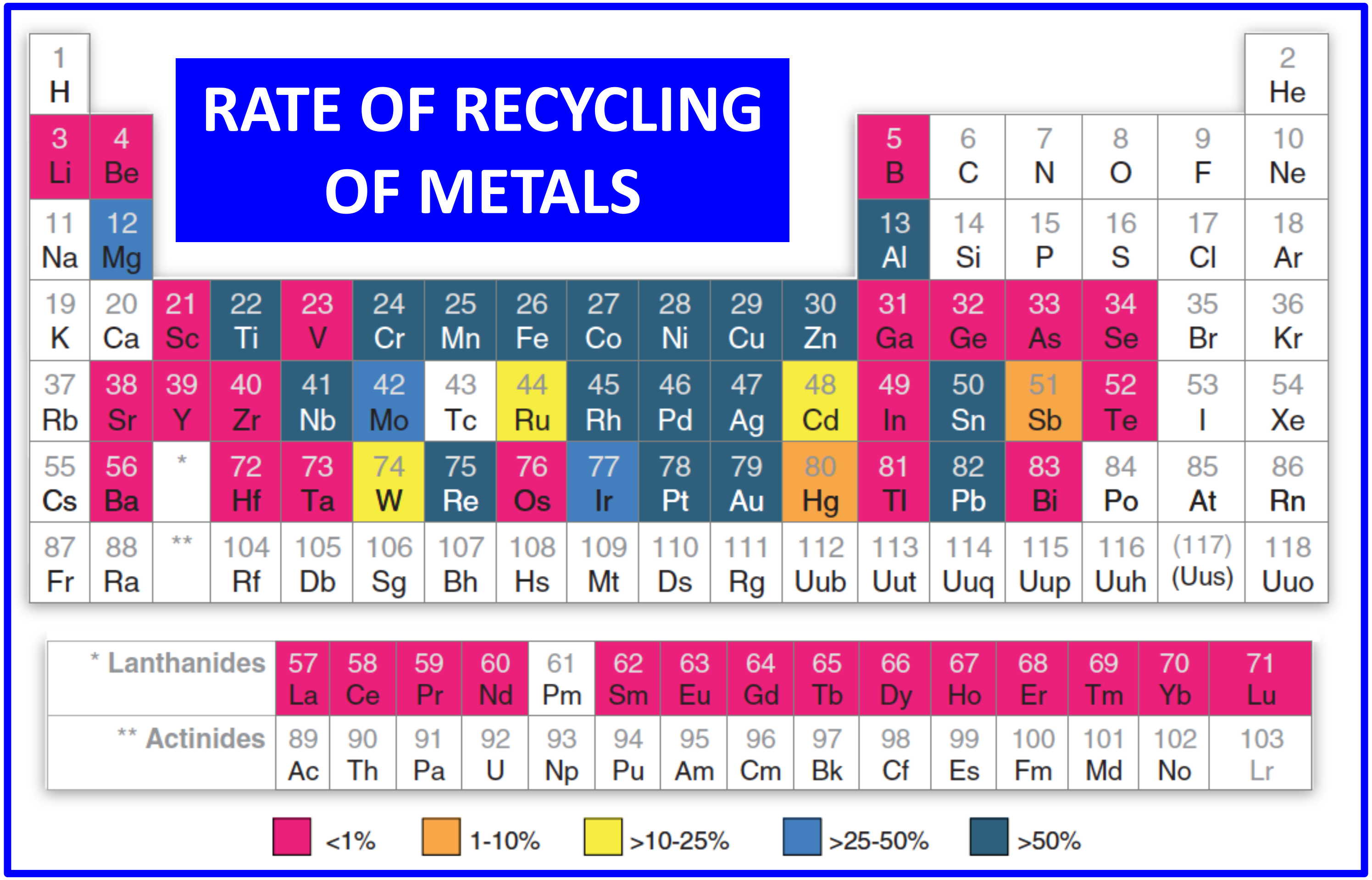
Photo Credit: National Geographic

CONCENTRATION (ppb)

	Earth	Asteroids
78 Pt Platinum 195.08	5	1400
77 Ir Iridium 192.22	1	760
46 Pd Palladium 106.42	15	870
79 Au Gold 196.967	4	215

This in NOT an option!

THE REAL ONE: RECYCLING



Science **2012**, *337*, 690

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

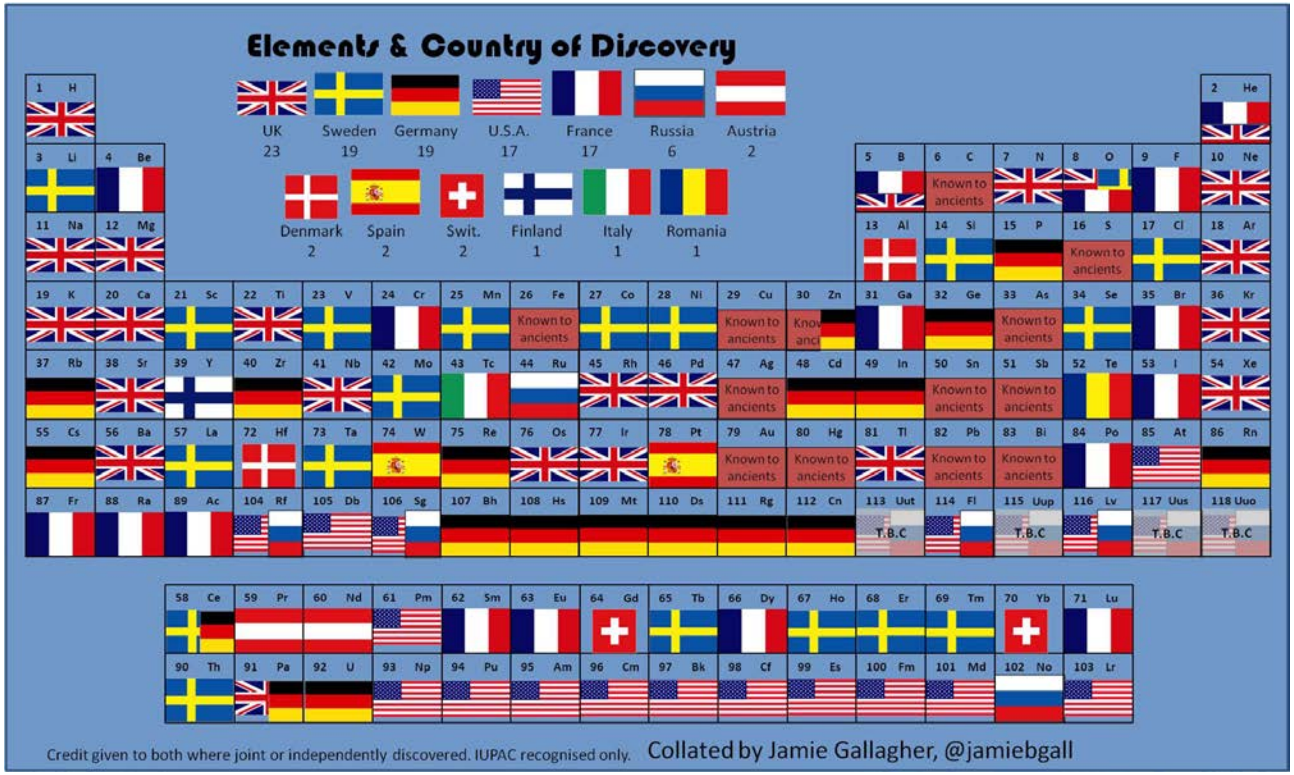
- On the contrary, all kinds of materials must be obtained from planet Earth, a sort of spaceship with limited resources in its hold

- 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

- <u>WARNING</u>. 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 …