

ENERGY FOR THE 21st CENTURY: WHERE WE ARE, WHERE WE SHOULD GO

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<http://www.isof.cnr.it/content/armaroli-nicola>



Chemistry for the Future of Europe - Energy, Food, Environment

University La Sapienza – Rome

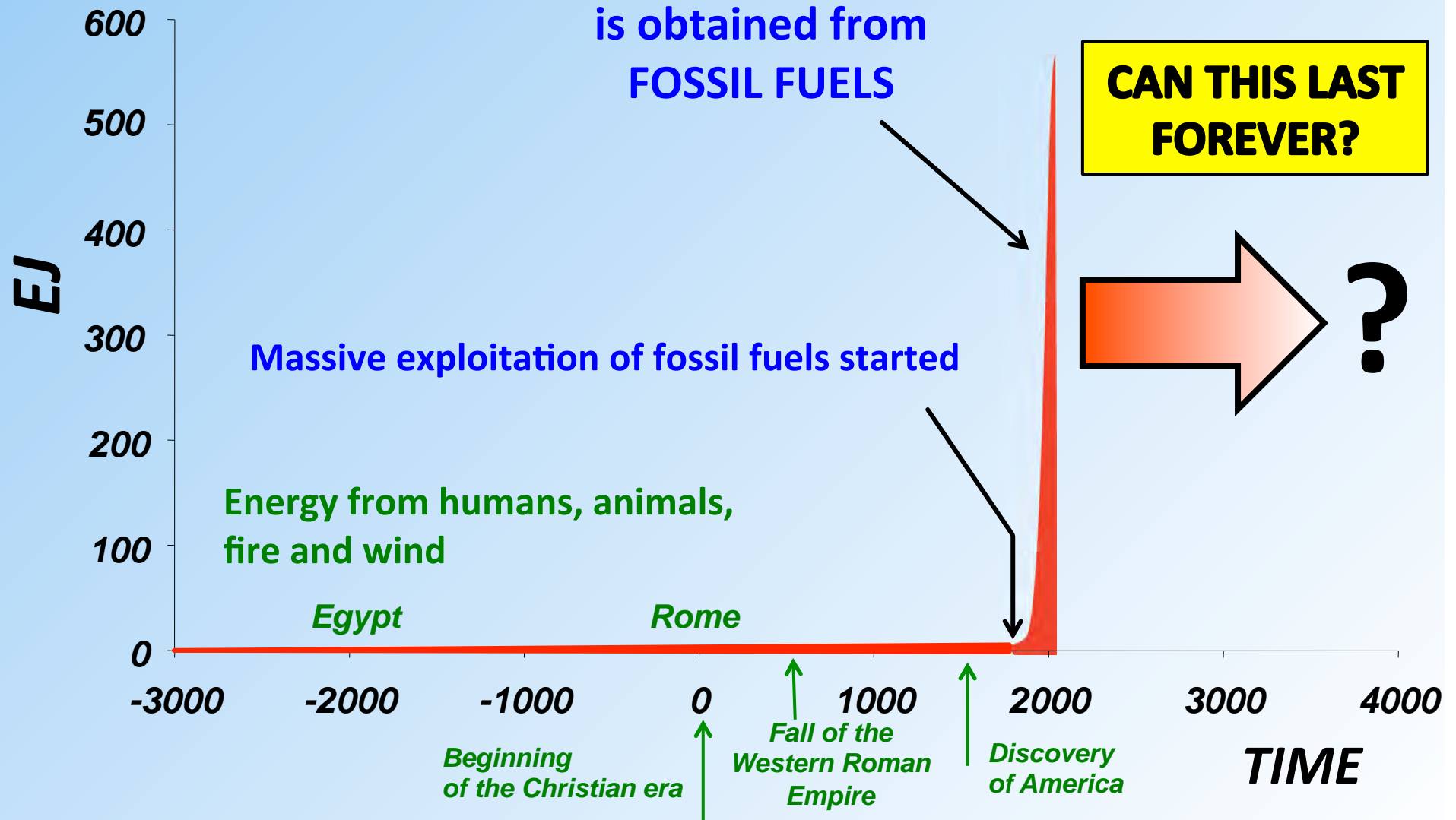
November 25, 2014

OUTLINE

- **PART I: The present situation**
- **PART II: The perspectives**
- **PART III: Reflections on Europe**

THE ENERGY TIMELINE

- 80% of this energy is obtained from **FOSSIL FUELS**



RUNNING TOO FAST: rate of consumption of fossil fuels

Consumption of fossil CARBON: $\approx 10 \text{ Gt/y}$

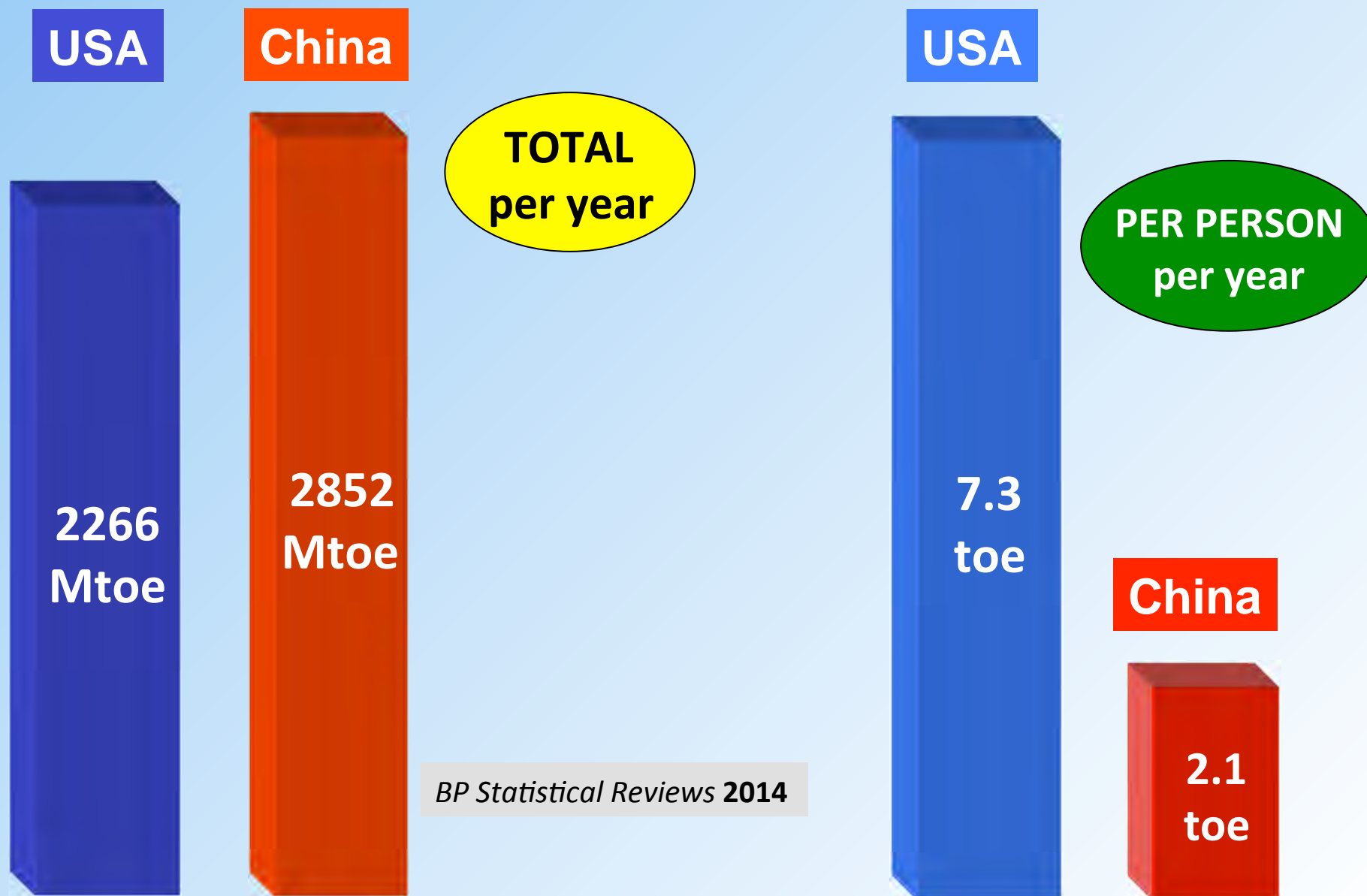


Amount of “paleobiomass” needed : $\approx 50\,000 \text{ Gt}$



This amounts to about
500 years of photosynthesis

The consumption race: USA vs. China



World oil reserves, top 10 countries

	Gigabarrels	%	} 62.0%
Venezuela	298.3	17.7	
Saudi Arabia	265.9	15.8	
Canada	174.3	10.3	
Iran	157.0	9.3	
Iraq	150.0	8.9	
Kuwait	101.5	6.0	
Un. Arab Emirates	97.8	5.8	
Russia	93.0	5.5	
Libya	48.5	2.9	
USA	44.2	2.6	

BP Statistical Reviews, 2014

Consequence : The most dangerous place on Earth

THE STRATEGIC ENERGY ELLIPSE



**16 countries, 70% of conventional
OIL and GAS reserves**

ENERGY is embodied everywhere

Steel

0.4*



Plastics

2.5*



Aluminum

4.2*



Motor vehicles

2.4*



Wheat, corn fruit

0.1*



Rice

0.25*



Greenhouse vegetables

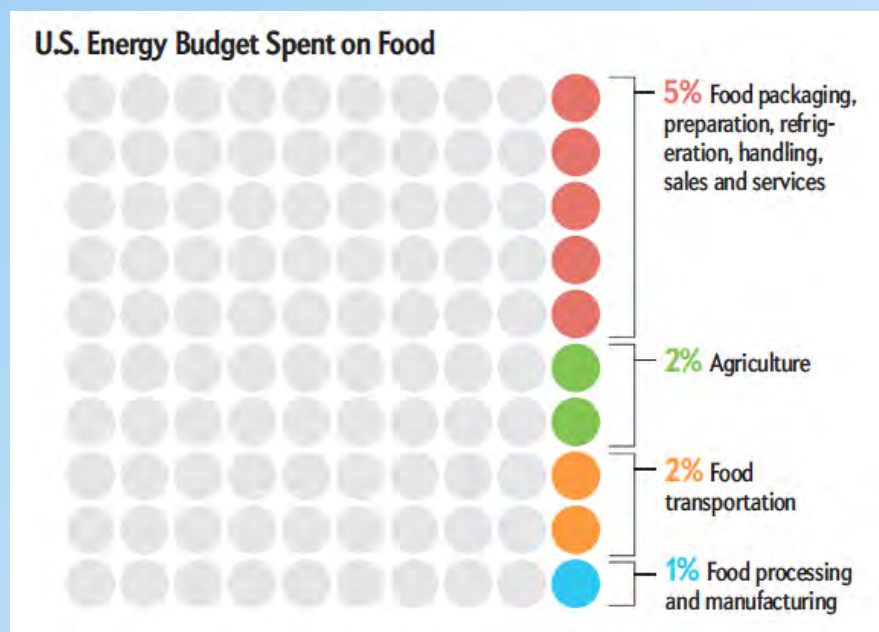
1*



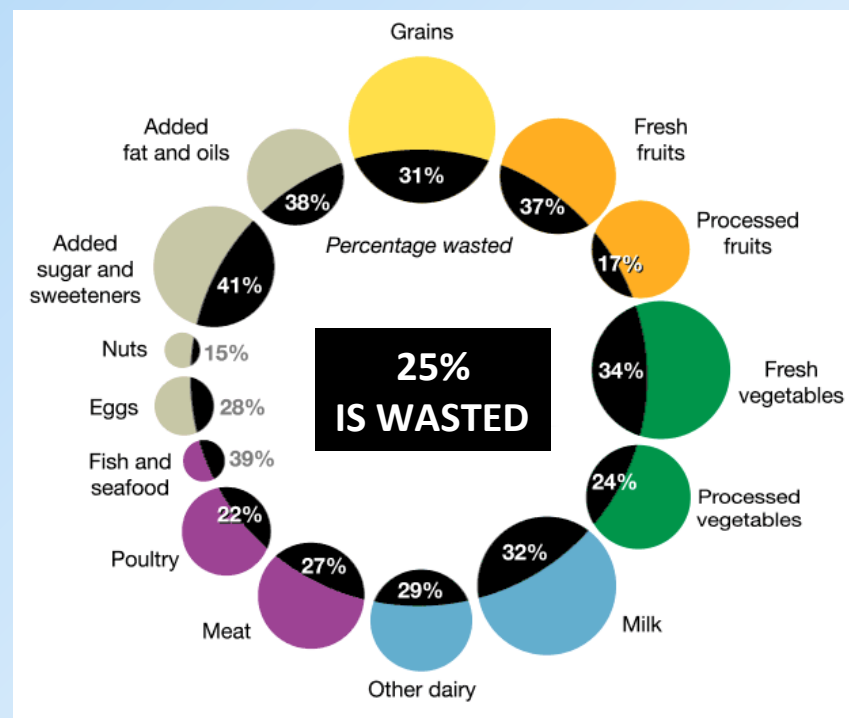
*toe/t

ENERGY is also wasted everywhere

10 % of U.S. energy is used to make food available



M. E. Webber, *Sci. Am.* January **2012**, 64



National Geographic Magazine, November **2014**
The Future of Food Features

2.5% of U.S. energy supply is wasted in food loss

Food wasted yearly by an average U.S. family



CREDIT: National Geographic Magazine, November 2014

ENERGY production requires huge amounts of WATER: the case of Europe

“The total abstraction of freshwater across Europe is around 288 km³/year* and represents, on average, 5 300 m³ per capita/year. Overall, 44 % of the total abstracted is for energy production, 24 % for agriculture, 21 % for the public water supply and 11 % for industry”

* Approx. SIX Garda Lakes

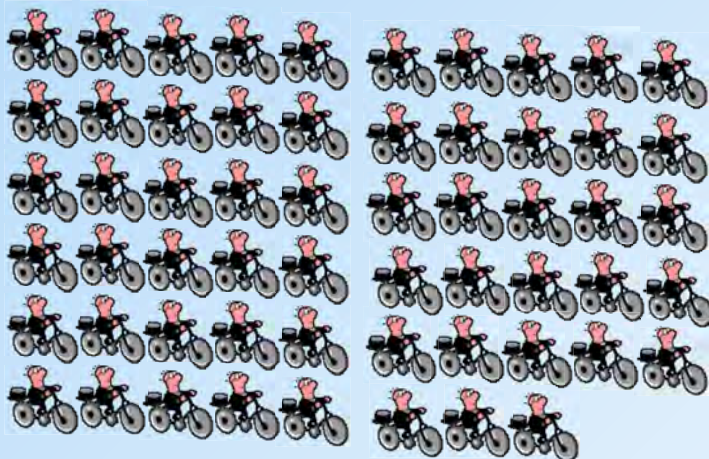
European Environment Agency, *Water resources across Europe. Confronting water scarcity and drought*, 2009

QUANTIFYING OUR FOSSIL FUEL BONANZA

THE “ENERGY SLAVE” POWER UNIT: STEADY 80 W FOR 8 HOURS



This guy is your
hypothetical slave



THE AVERAGE EU CITIZEN
HAS 58 ENERGY SLAVES
WORKING 24/7
AND NO HOLIDAYS

IS ENERGY REALLY EXPENSIVE?

Mmm .. let's make a quick calculation

EU AVERAGE HOUSEHOLD
ELECTRICITY CONSUMPTION

3500 kWh

EU AVERAGE ELECTRICITY
CONSUMPTION FOR LIGHTING

14%



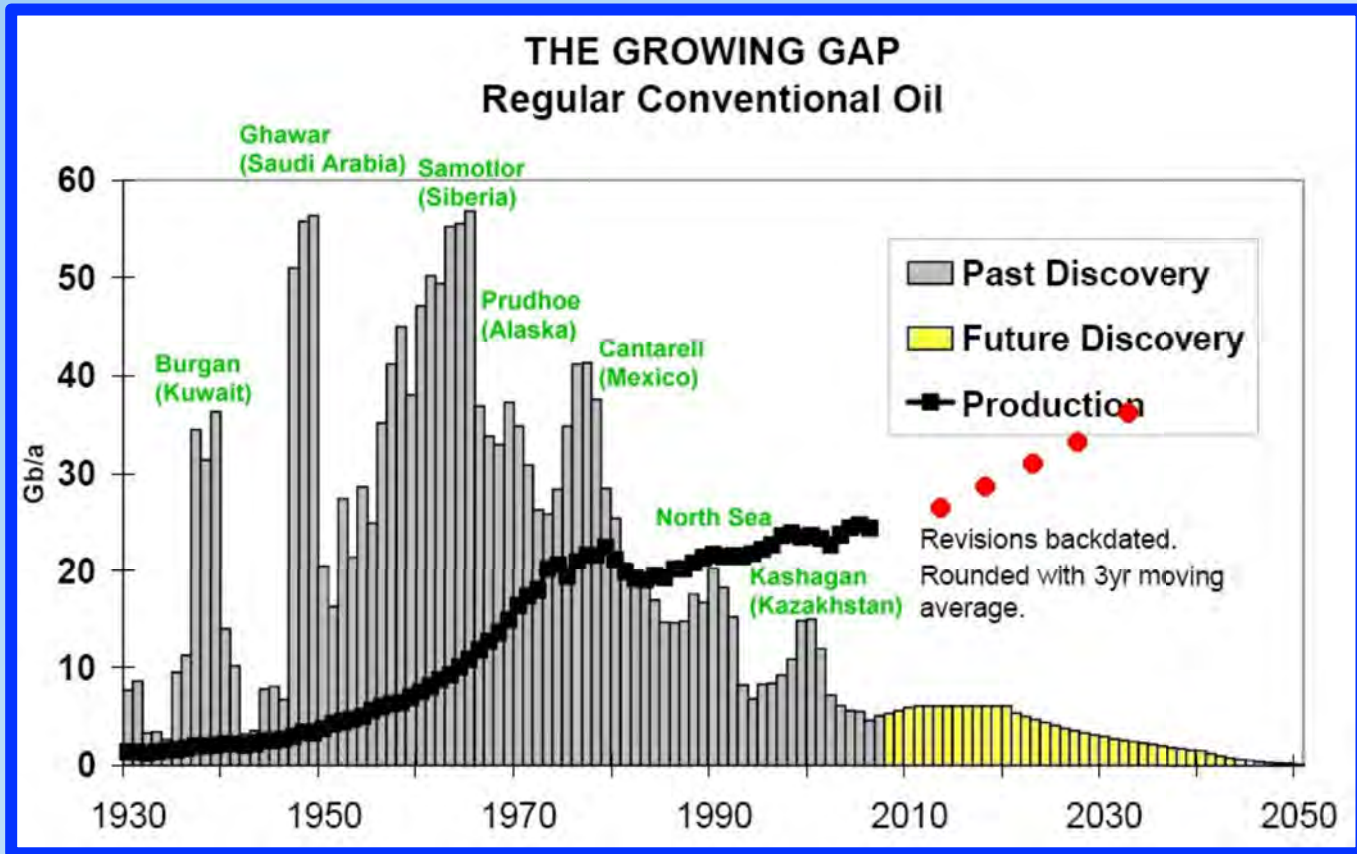
490 kWh

98 €

490 kWh = 766 people for 10 h

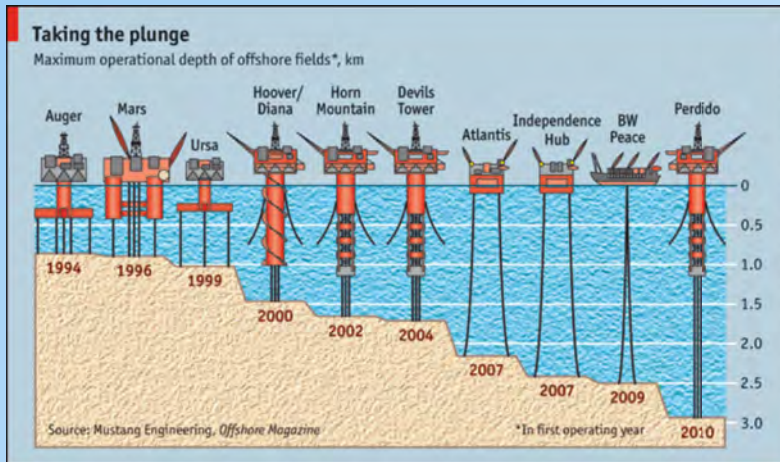
230.000 € (at 30 €/h)

The dwindling resource: CONVENTIONAL OIL discoveries vs. production, historical



The future of oil supply
- Special Issue -
January 2014

Entering the era of “extreme” oil & gas



C&EN, Feb 14, 2011

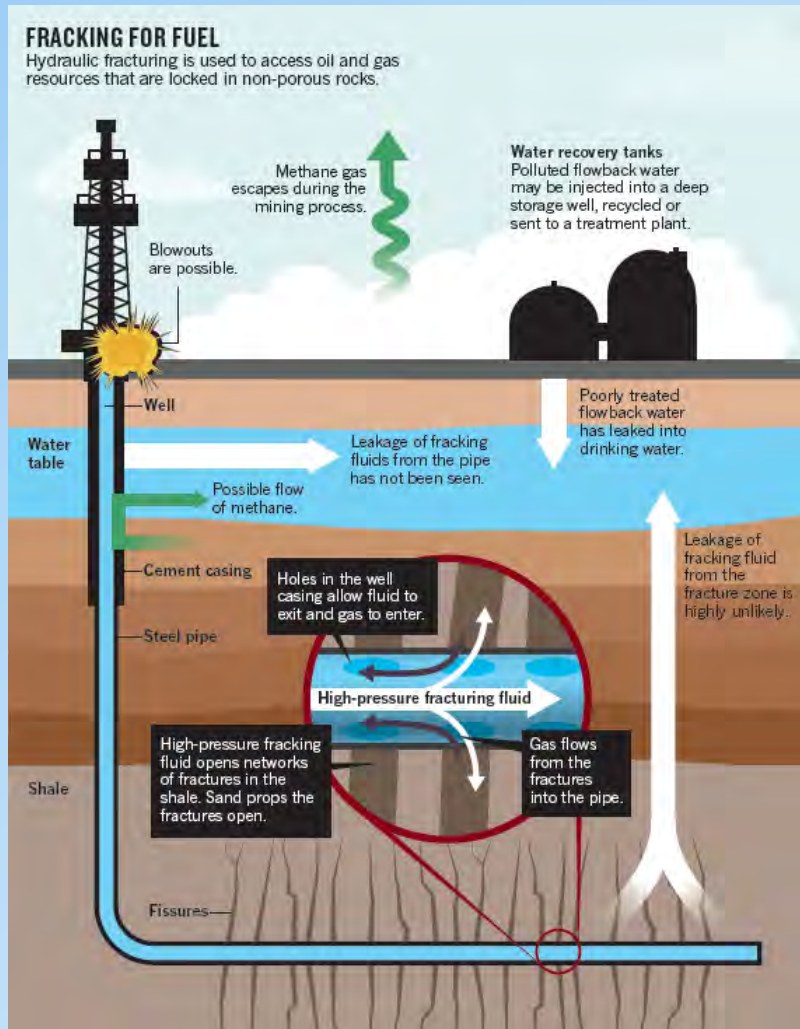
Deep sea and
Arctic drilling



Unconventional
hydrocarbons:
- Tar sands,
- Shale oil & gas

“FRACKING” FOR SHALE OIL & GAS:

Associated Risks and Problems



Nature **2011**, 477, 271

Groundwater Contamination

Science **2014**, 344, 1468

PNAS **2013**, 110, 11250

Nature **2013**, 498, 415

Induced Seismicity

Science **2013**, 341, 142

U.S. NAS Report **2012**, ISBN 978-0-309-25367-3

Methane release in the atmosphere

PNAS **2014**, 111, 6237

Nature **2012**, 482, 139

Quickly declining rate of production

Nature **2012**, 494, 307

Poor EROI

Environ. Sci. Tech. **2013**, 47, 5459

Key concept: IT TAKES ENERGY TO GET ENERGY
(ENERGY RETURN ON ENERGY INVESTMENT: EROEI)



EXAMPLE: EROEI U.S. oil

1950

100

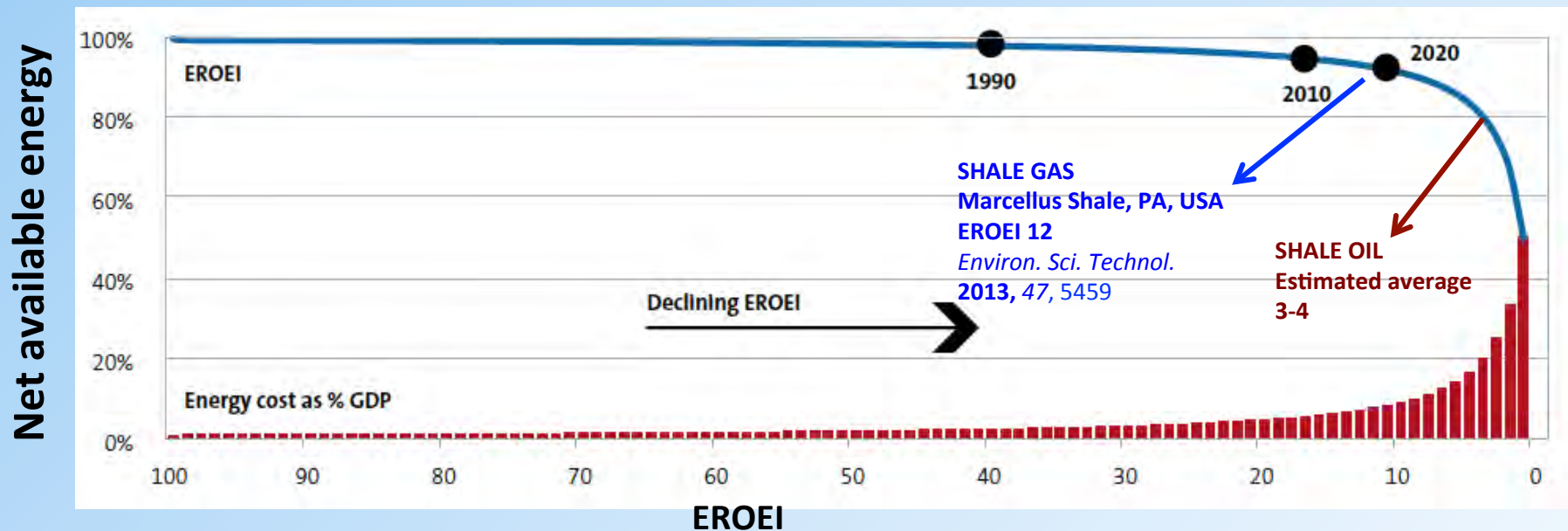
1970

30

Today

< 10

APPROACHING THE EROEI CLIFF?



Some financial analysts estimate that with EROEI below ≈ 10 the world economy is poised to collapse

Perfect Storm - Energy, Finance and the End of Growth
Tullet Prebon Report, **2013**

SHALE OIL AND GAS: THE NEXT BUBBLE?

Newsweek

Is the U.S. Fracking Boom a Bubble?

July 14, 2014

Bloomberg

Drillers Piling Up More Debt Than Oil Hunting Fortunes in Shale


September 8, 2014

The Telegraph

Shale gas: 'The dotcom bubble of our times'

Comment: output from shale wells declines so quickly that they will never be profitable – when investors realise this, the industry will collapse, writes Tim Morgan

August 04, 2014

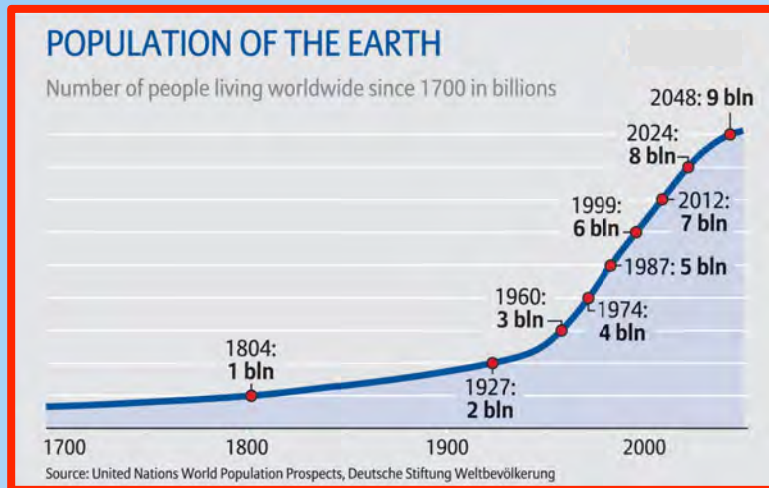
 **Il Sole
24 ORE**

**Crollo del petrolio e debito
spazzatura,
la bolla dello shale oil rischia di
esplodere**

November 12, 2014

OTHER (SOME) RELATED BIG ISSUES

GLOBAL WARMING



Trend: + 80 million/year, + 220 000/day



<http://climate.nasa.gov/sof/>

ENVIRONMENTAL DEGRADATION



PO VALLEY
October 30, 2014

<http://earthobservatory.nasa.gov>

**THE PERFECT
STORM?**

The last 80 years: the fossil fuel age

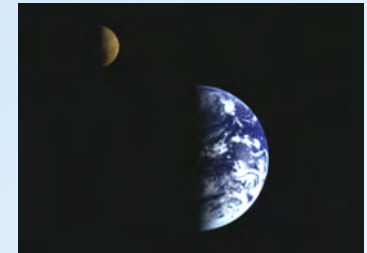


**BUT ... CONVENTIONAL HYDROCARBONS WILL BE
VIRTUALLY IMPOSSIBLE TO REPLACE**

OUTLINE

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- **PART III: Reflections on Europe**

How many renewable/perennial alternatives do we have??

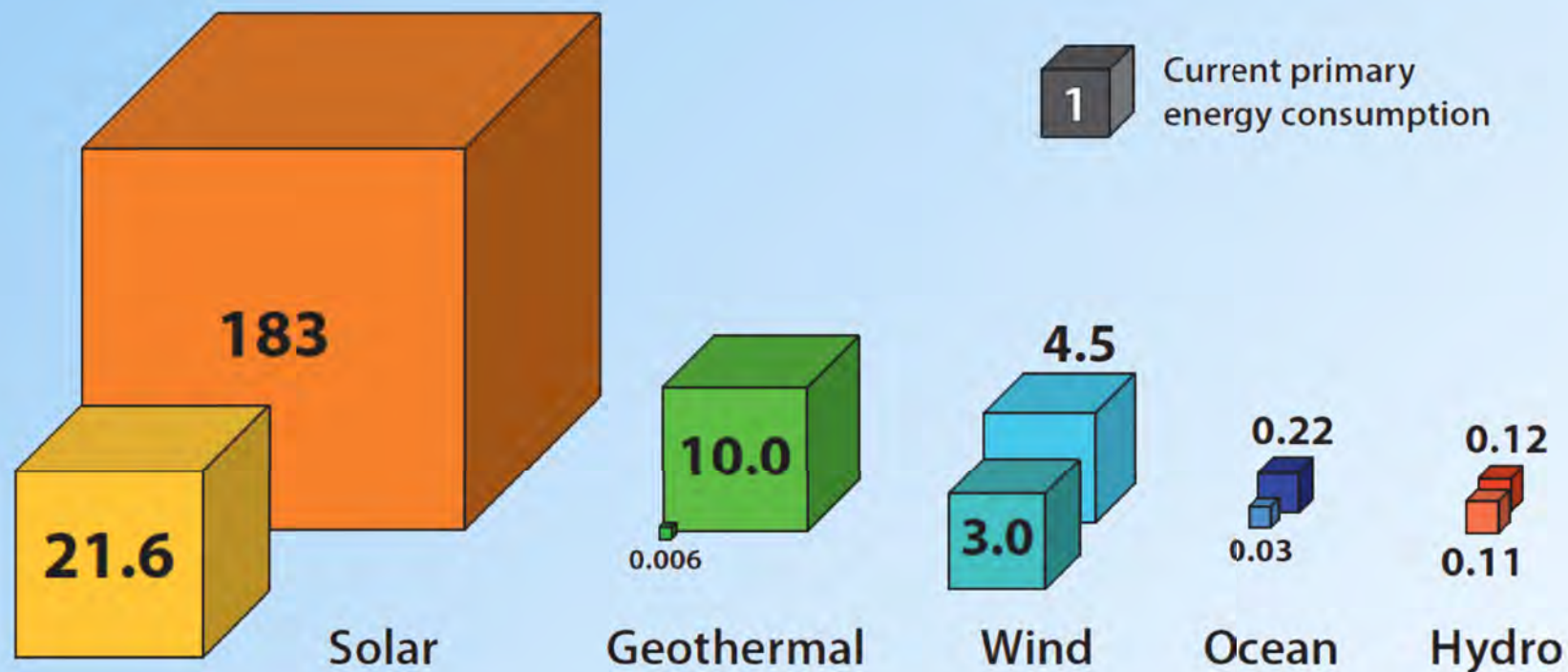


GEO THERMAL

GRAVITATIONAL

SOLAR
(DIRECT and INDIRECT)

Do we have enough? YES, INDEED



SMALLER CUBES: Amount that is technically, economically and ecologically exploitable NOW

N. Armaroli, V. Balzani
Energy for a Sustainable World, Wiley-VCH, **2011**

LET'S BE PRACTICAL: WHAT DO WE NEED?

Share of Final Energy Consumption
in the Affluent World



~ 25 %

ELECTRICITY



**FUELS
(heat, transport)**

~ 75 %

WE HAVE 2 OBJECTIVES

... WELL ... 3

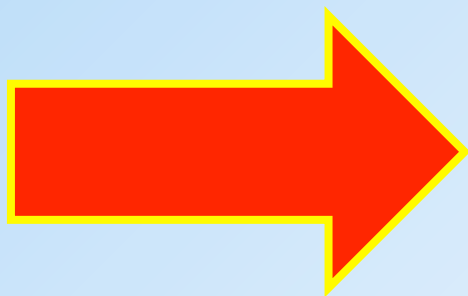
- 1) Produce ELECTRICITY**
- 2) Produce FUELS**
- 3) Reduce CONSUMPTION,
increase EFFICIENCY**

a) Target ELECTRICITY

The most mature renewable technologies are electric:

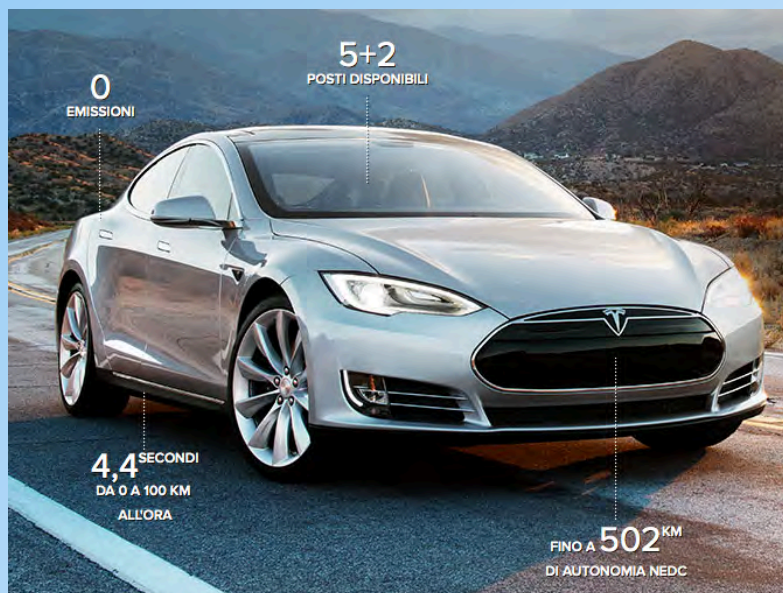


**INCREASE THE SHARE OF
ELECTRICITY IN FINAL USE**



Energy Environ. Sci. **2011**, 4, 3193-3222

HOW MUCH ELECTRICITY TO POWER e-CARS?



CONSUMPTION: **0.18 kWh/km**

15 000 km/year: **2700 kWh**

= MY HOUSEHOLD CONSUMPTION (5 people)

In Italy: **37 million cars**

Average mileage: **12000 km/year**

If electric they'd consume: **80 TWh**
(luxury, not economy car!)

Italy, 2013: **112 TWh from RENEWABLES** (ca. 40% of total cons.)



47%



19%



15%

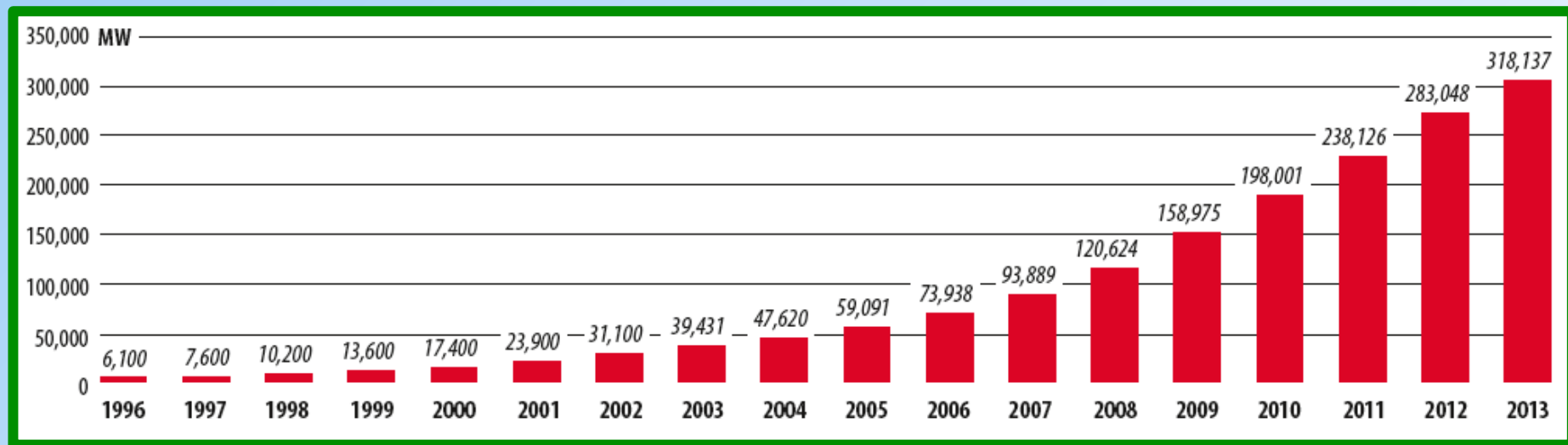


14%



5%

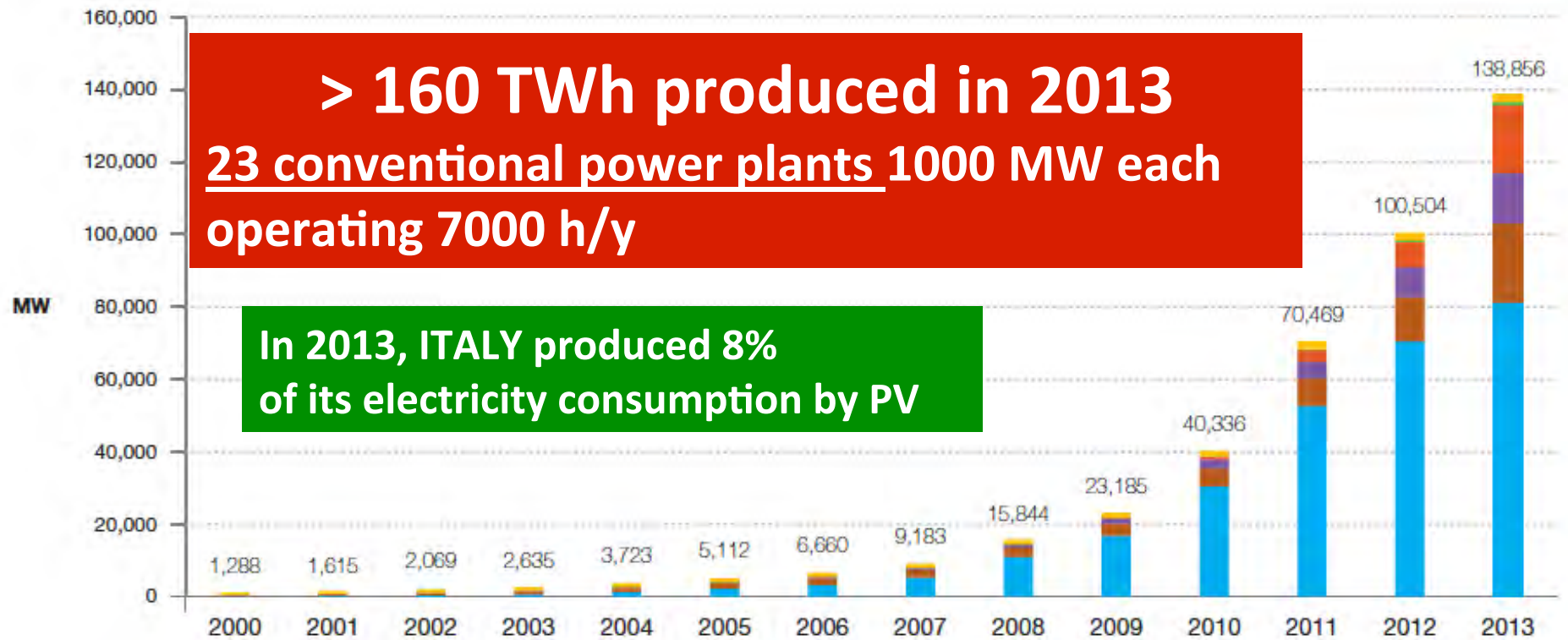
World development of WIND ENERGY, 1996-2013



2013: 596 TWh, 3.3% of world electricity
85 conventional power stations 1000 MW 7000 h/y

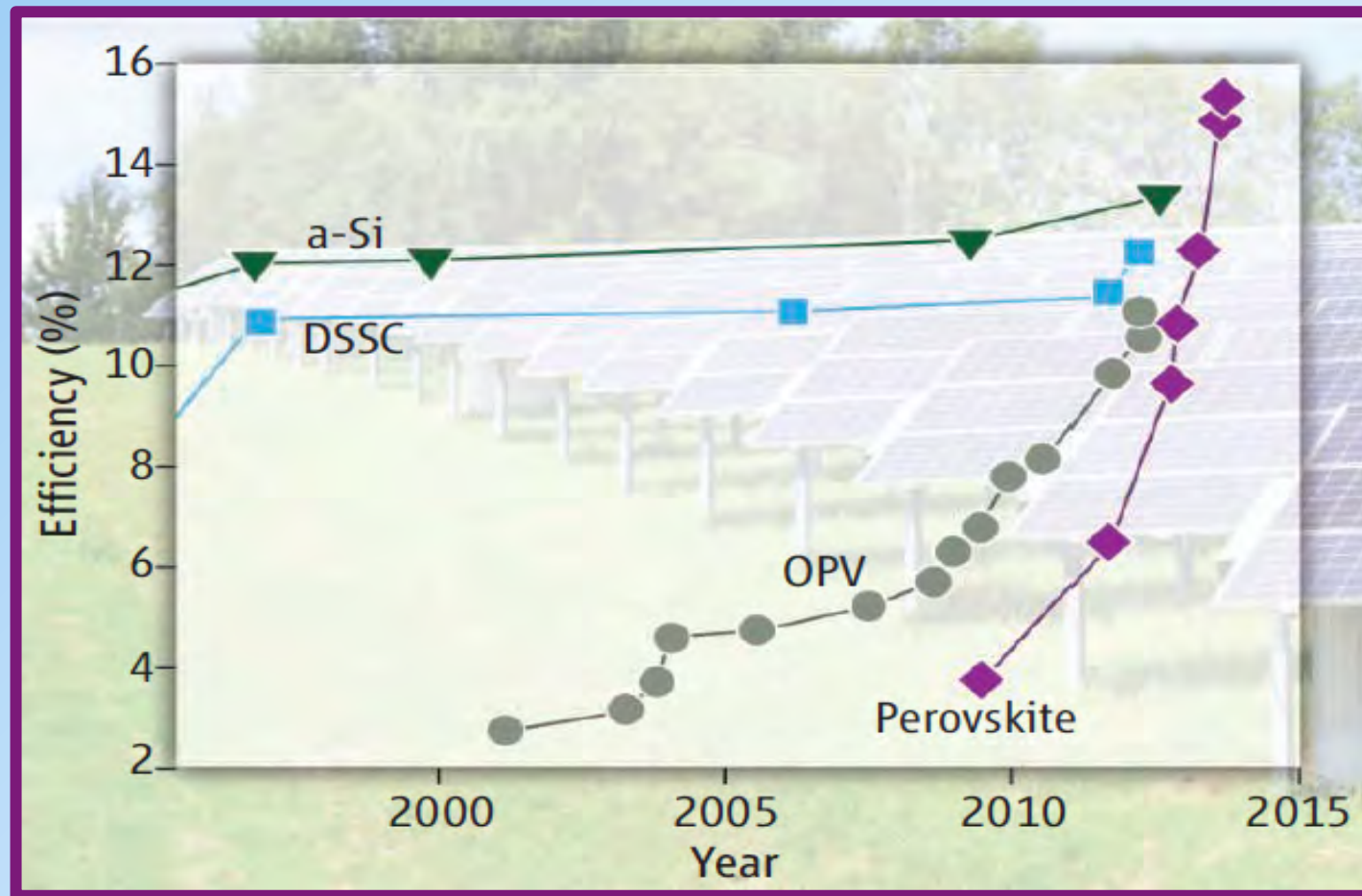
GWEC – Global Wind Energy Council, 2014

World development of PV ELECTRICITY, 2000-2013



EPIA Report, 2014

Potential competitors for crystalline silicon?



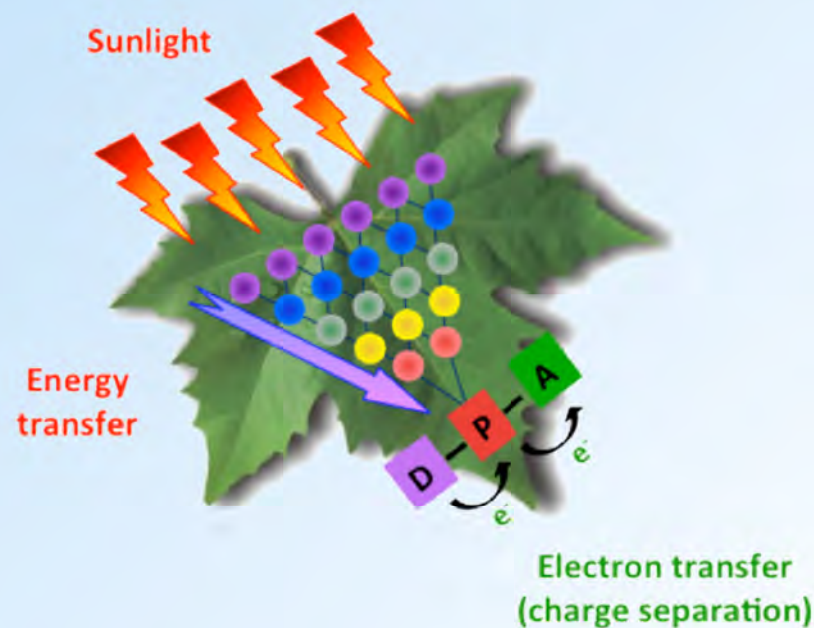
Perovskite-Based Solar Cells: $(\text{CH}_3\text{NH}_3)\text{MX}_{3-x}\text{Y}_x$ ($\text{M} = \text{Pb}/\text{Sn}$; $\text{X}, \text{Y} = \text{I}/\text{Br}/\text{Cl}$)

BIGGEST CHALLENGES for intermittent renewable electricity

- 1) **OVERCAPACITY** (installed capacity 2/3/4 x compared to conventional technologies)
- 2) **STORAGE**: peak production is often too large
- 3) **ELECTRIC GRID**: to be completely reshaped (*smart grid*)

b) Target FUELS

FROM THE EXPLOITATION
of naturally occurring (**fossil**) fuels
TO THE MANUFACTURING
of **artificial** fuels



Harvesting solar energy through natural photosynthesis:

BIOFUELS (4% of world's transportation fuels - 23% in Brazil)

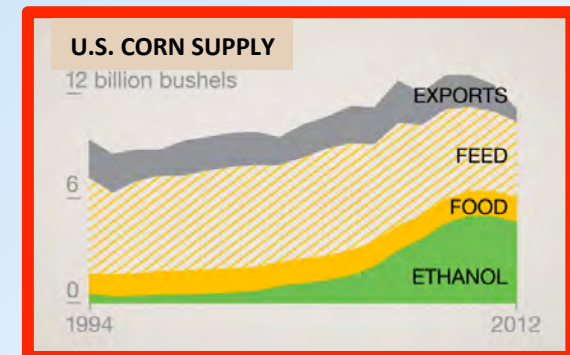
BIOETHANOL for **petrol** engines
(from corn, sugarcane,
sugar beet, sorghum)



BIODIESEL for **diesel** engines
(from vegetal oils: rape,
sunflower, soybean, palm, etc.)



1ST GENERATION



BIOETHANOL from non edible
cellulosic materials and
non food crops



2ND GENERATION

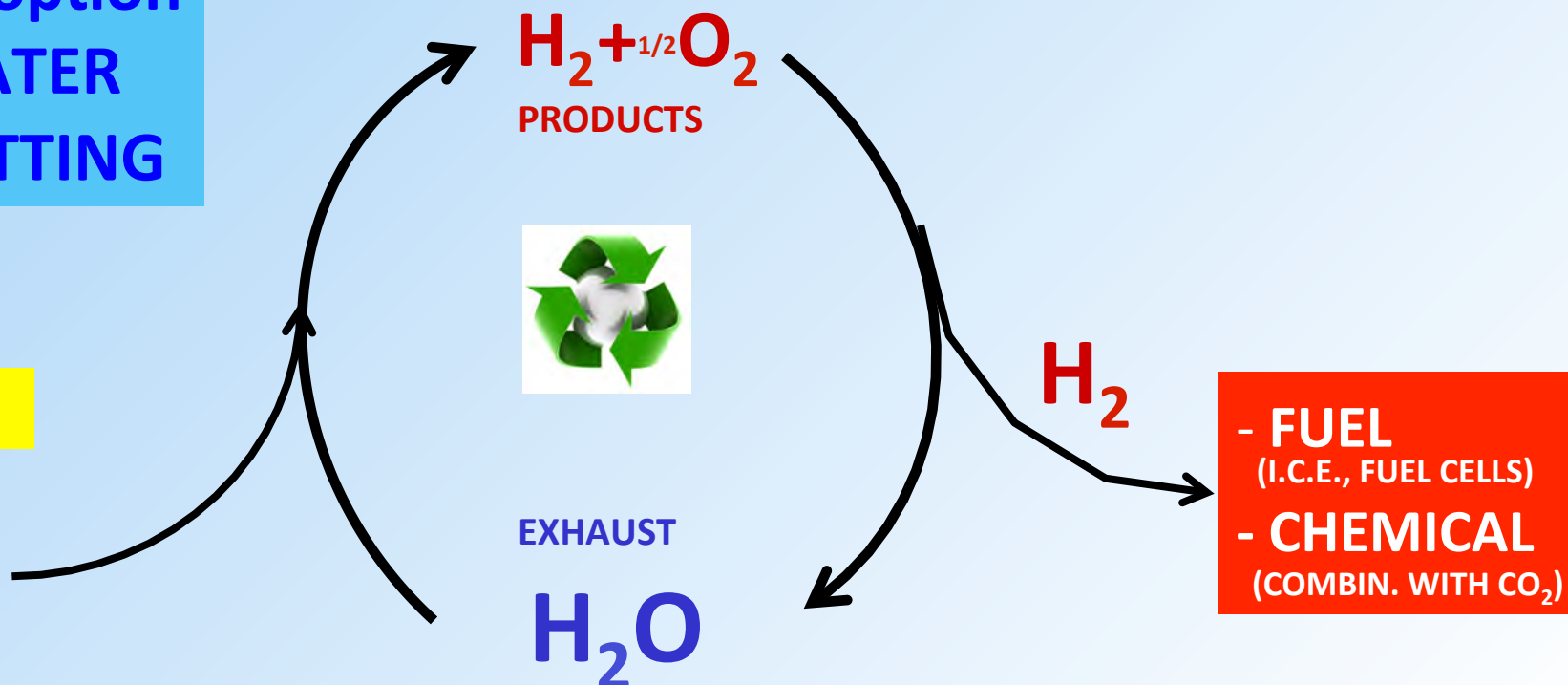
COMING UP

3RD GENERATION SOLAR FUELS: ARTIFICIAL PHOTOSYNTHESIS

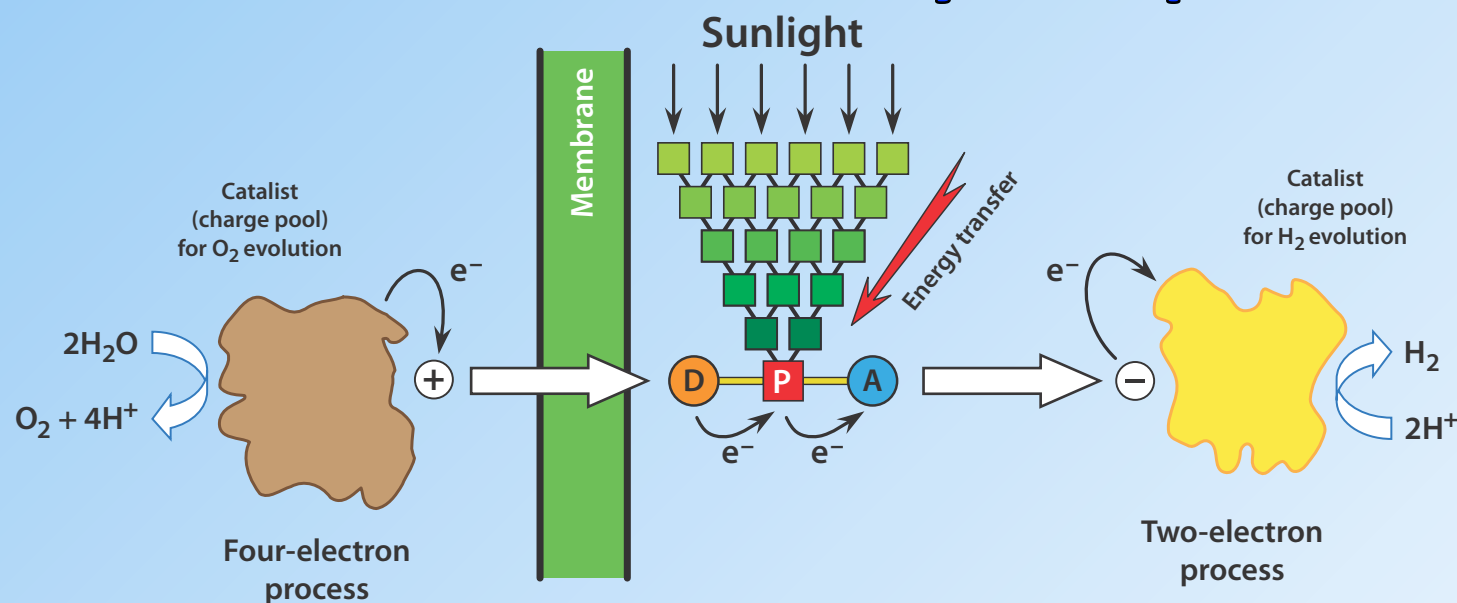


Best option
WATER
SPLITTING

SUNLIGHT



WATER SPLITTING - key components



1) Antenna (energy transfer)

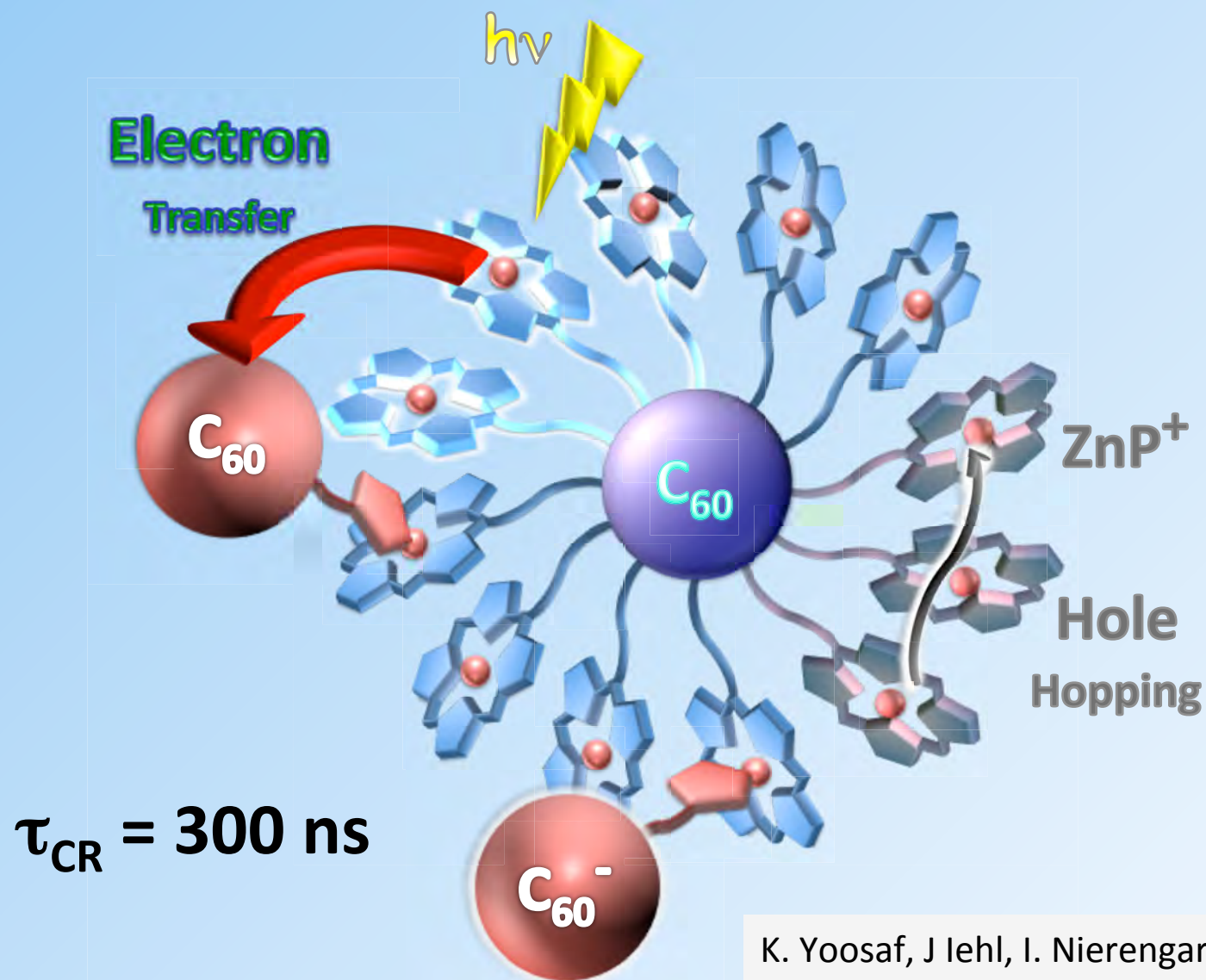
2) Charge separation unit (electron transfer)

3) Catalyst for H_2 evolution

4) Catalyst for O_2 evolution

5) Membrane separating the two processes

A supramolecular model photosynthetic antenna/CS unit



K. Yoosaf, J. Iehl, I. Nierengarten, M. Hmadeh, A.-M. Albrecht-Gary, J.-F. Nierengarten, N. Armaroli
Chem. Eur. J. **2014**, *20*, 223-231

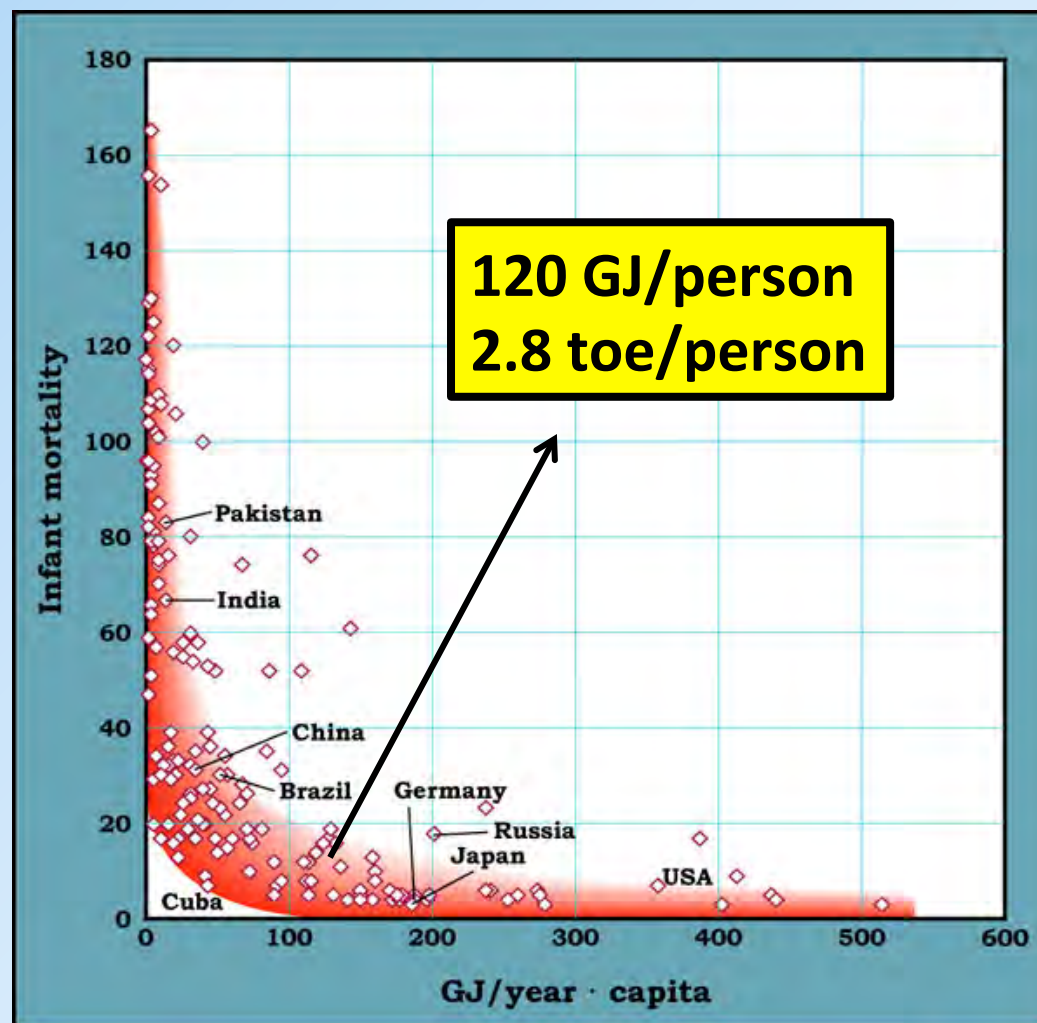
c) Target REDUCED CONSUMPTION and INCREASED EFFICIENCY



Reducing consumption: HOW MUCH?

**Infant
mortality**

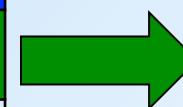
A parameter strictly
related to the quality
of life



Credit: Prof. Vaclav Smil, Univ. of Manitoba, CANADA

Energy consumption: an ideal path to 2050

	Mtoe/country	toe/pers
Canada	333	9.4
USA	2 266	7.3
France	248	3.8
EU	1 760	3.5
Italy	159	2.6
TARGET 2050	25 000	2.8
China	2 852	2.1
WORLD 2013	12 730	1.8
Brazil	284	1.4
India	595	0.5
Ethiopia	3	0.03



2050
9 billion



2013
7.2 billion

Elaborated from Eurostat, PRB, and BP Statistical Reviews 2014

What would you do with 0.03 toe/y of energy?



Improving EFFICIENCY: lighting



40%



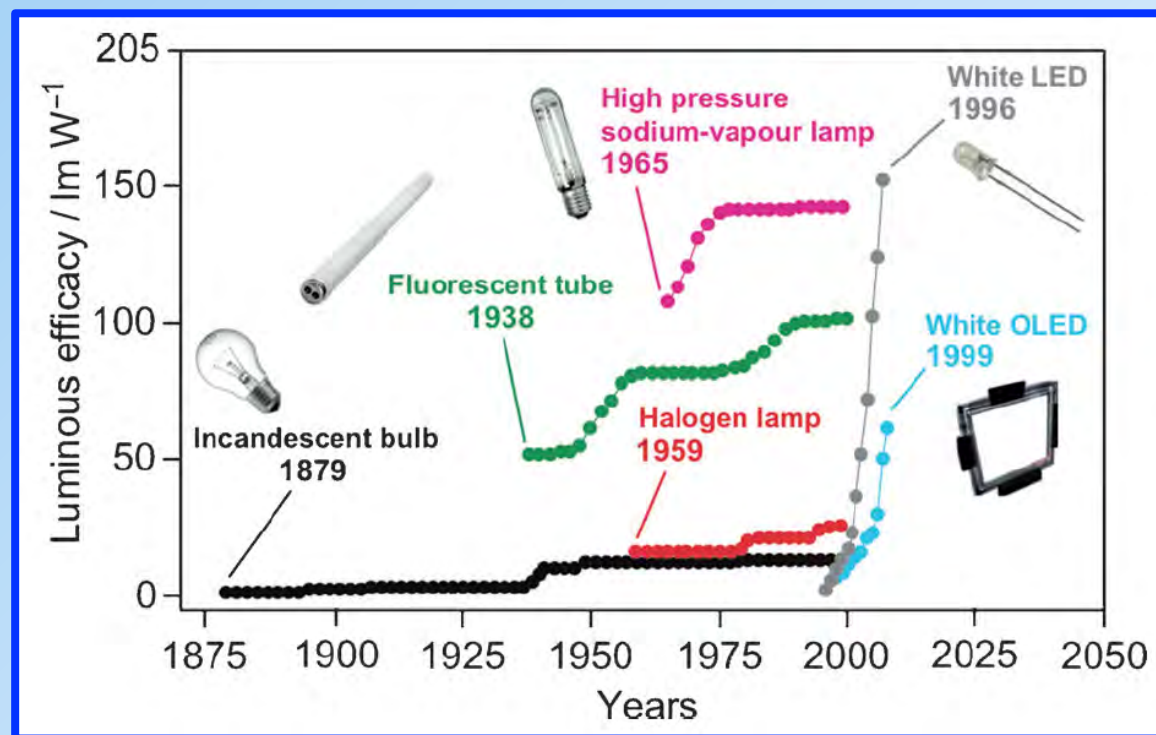
95%



22%

Overall Efficiency < 10%

Ongoing epochal change in lighting



“OLD” TECHNOLOGIES

hot lighting

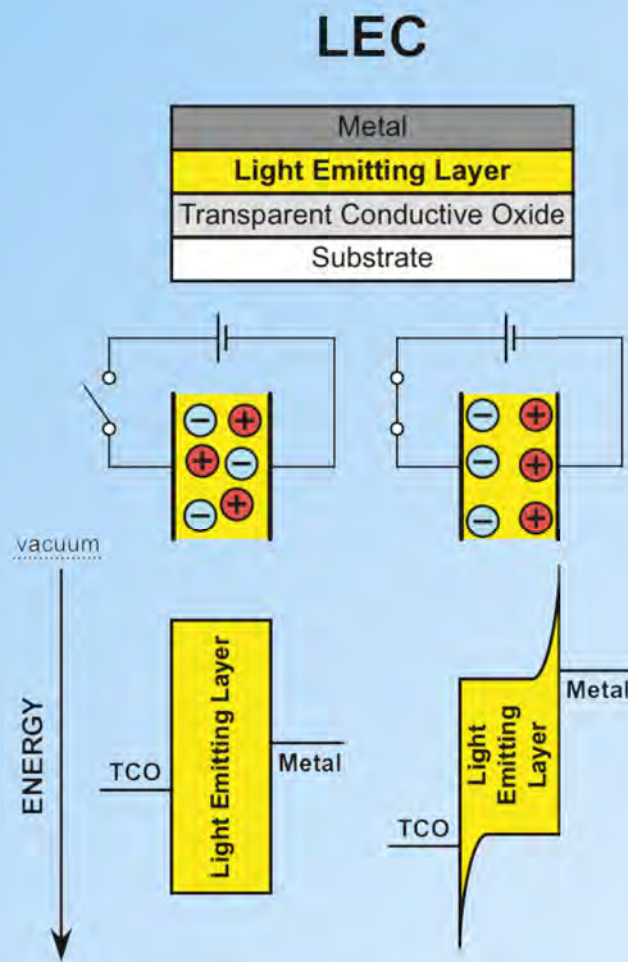
Light is an indirect effect

LED and OLED

cold lighting

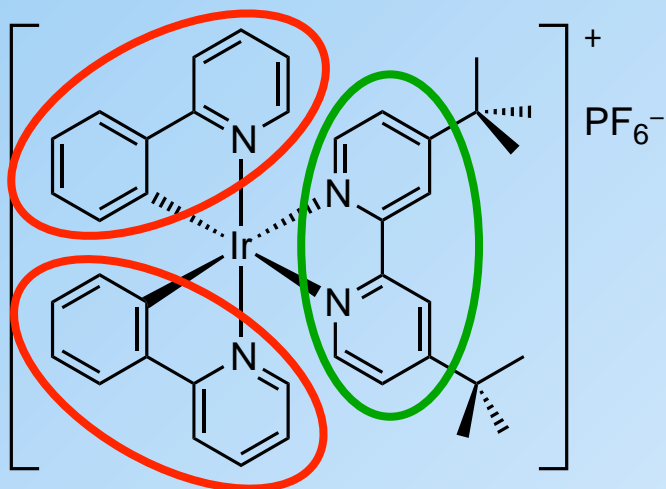
Materials/molecules are
the very emitters

A simpler design concept than OLEDs: LIGHT EMITTING ELECTROCHEMICAL CELL (LEC)



- ✓ ionic metal complexes
- ✓ few layers
- ✓ easy processability

Mostly investigated iTMCs for LECs: Ir(III)



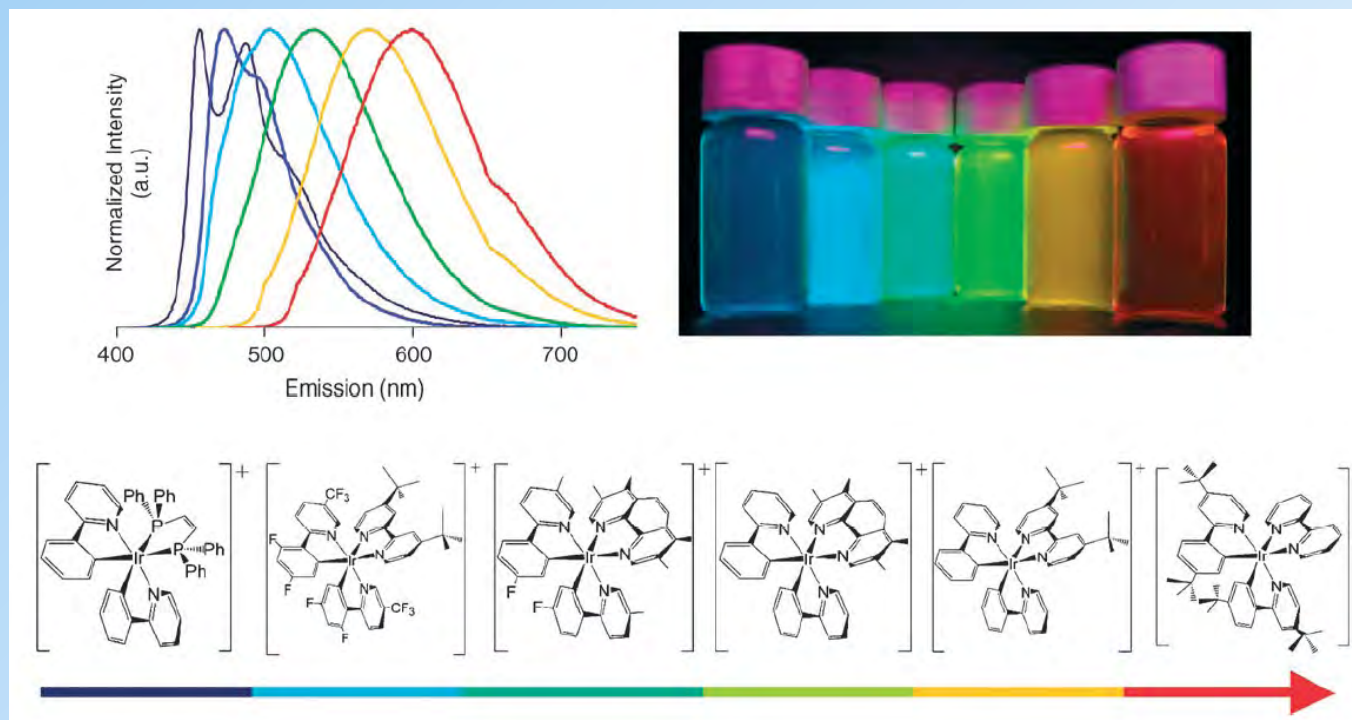
Cyclometallating C-N ligands

“Ancillary” N-N ligand

R. D. Costa, E. Ortì, H. J. Bolink, F. Monti, G. Accorsi, N. Armaroli
Angew. Chem. Int. Ed. **2012**, 51, 8178–8211

Ir(III) complexes

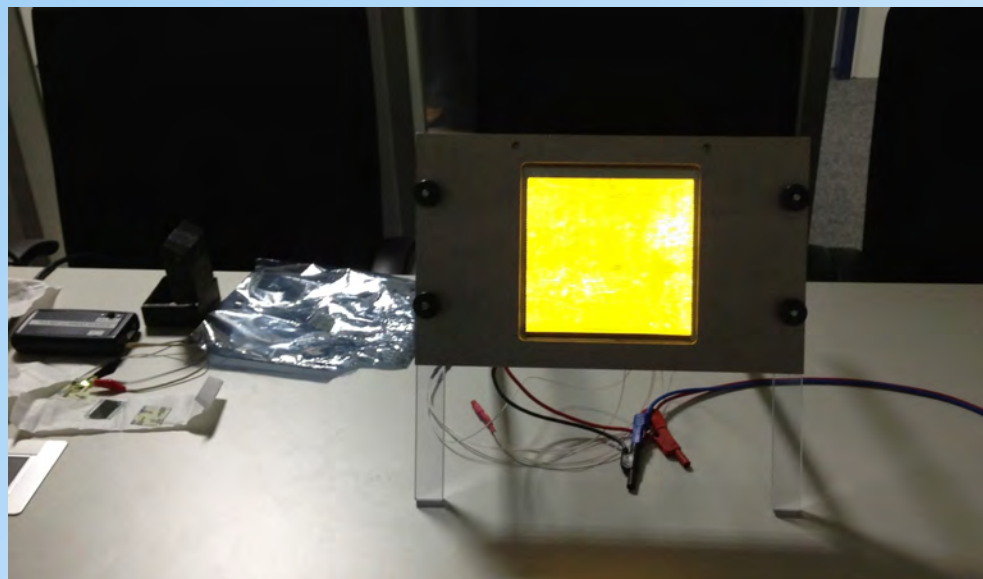
emission from blue to red by ligand design



Chem. Eur. J. 2006, 12, 7977

Luminescence always stems from the lowest TRIPLET excited state
HOMO-LUMO energy tuning allows colour change

LEC demonstrator



Size: **210 cm²**

Brightness: **1150 cd/m²**

Efficacy: **4.5 lm/w**

VNIVERSITAT
ID VALÈNCIA

SIEMENS



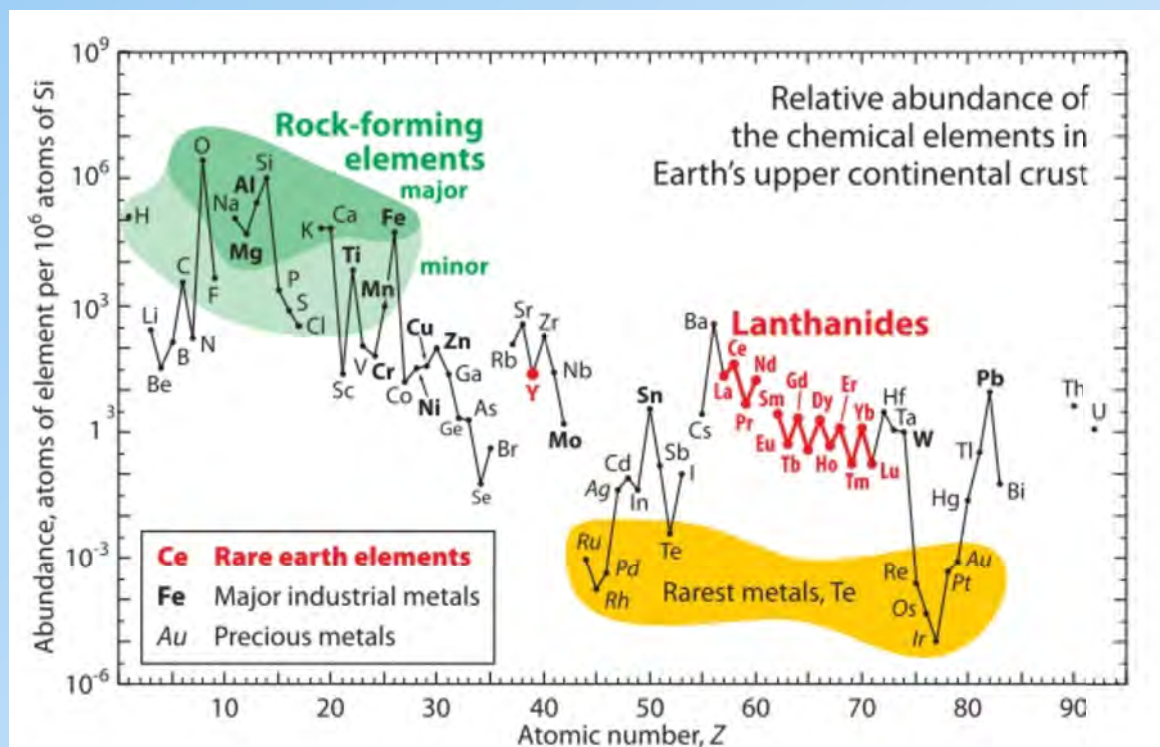
ISOF
CNR



OSRAM

VTT

Iridium is great, but there is a problem



The rarest element on Earth's crust ...

World Iridium production is around 4 t/y
($\approx 6 \times 10^{-4}$ g/person)

Possible alternatives to Ir(III) complexes

Periodic Table of the Elements

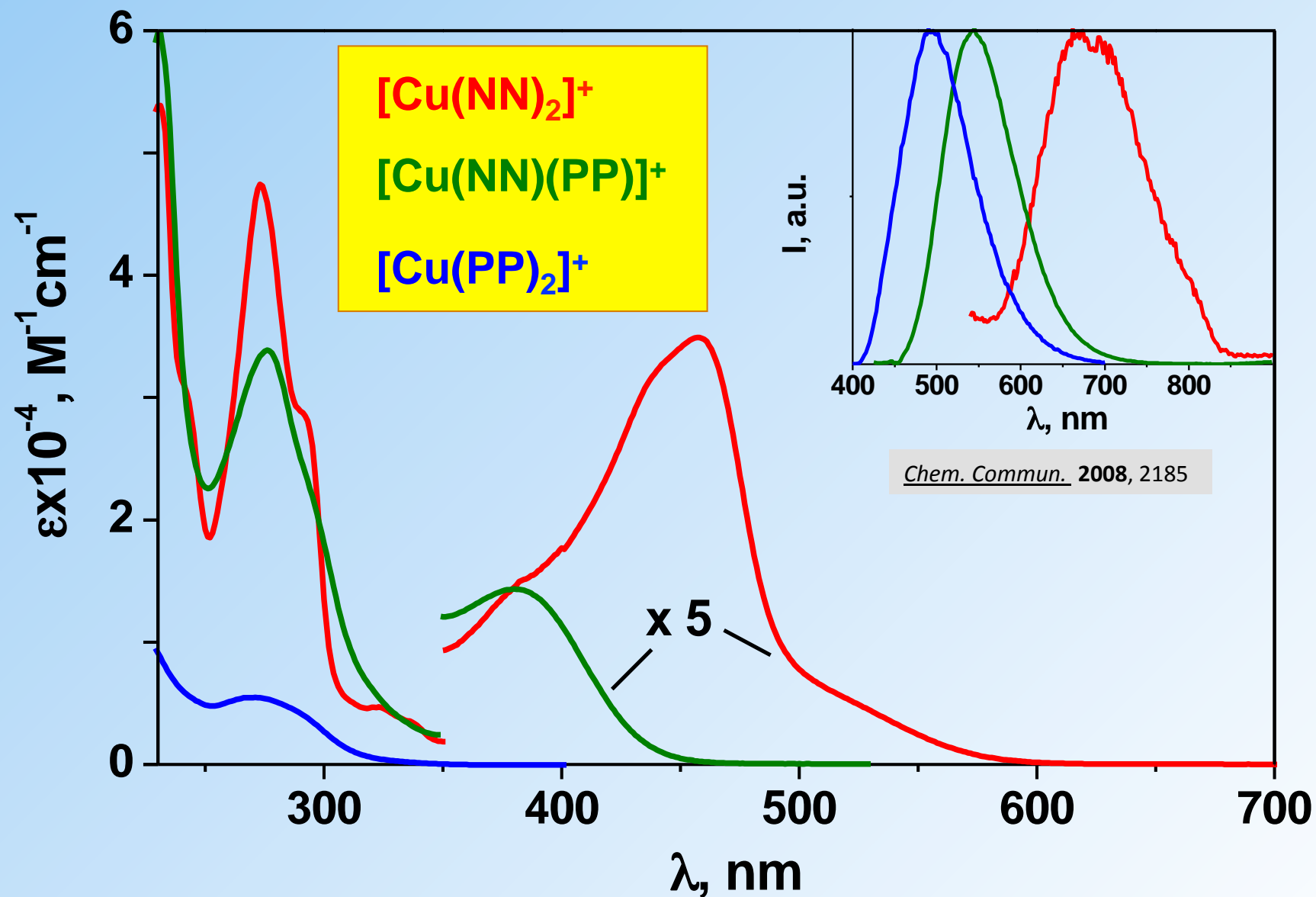
1A																	0													
1	H																	2	He											
2	Li	Be																	5	B	6	C	7	N	8	O	9	F	10	Ne
3	Na	Mg																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr												
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe												
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn												
7	Fr	Ra	+Ac	Rf	Ha	Sg	Ns	Hs	Mt	110	111	112	113																	

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

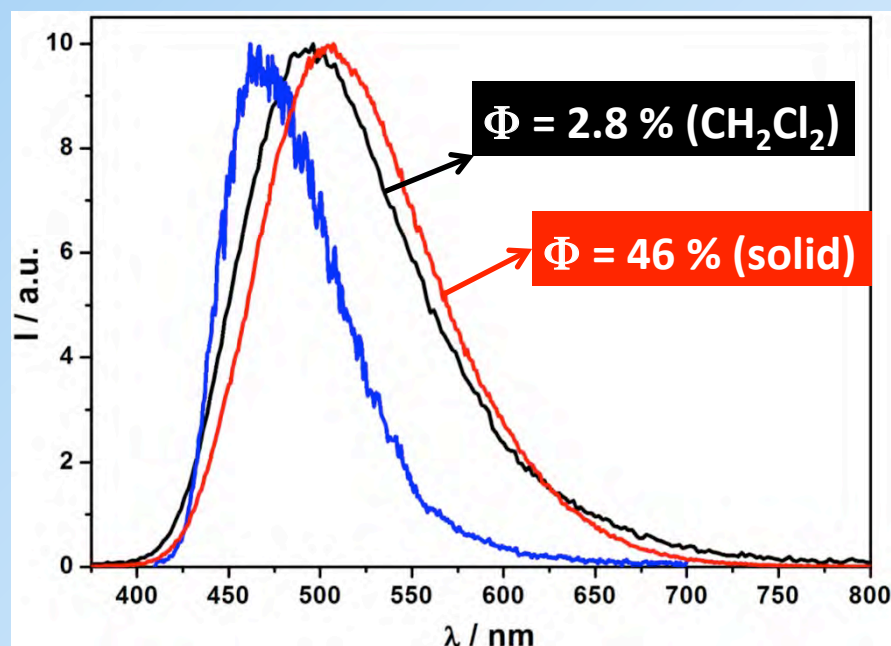
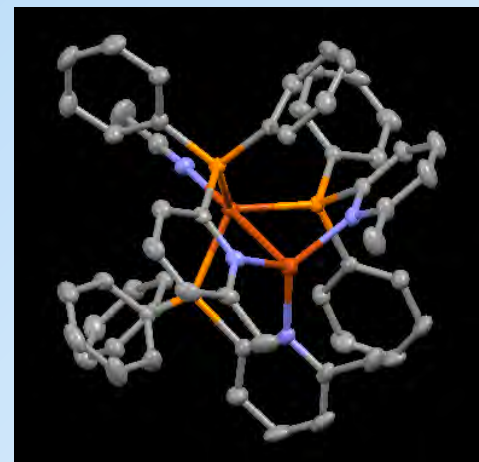
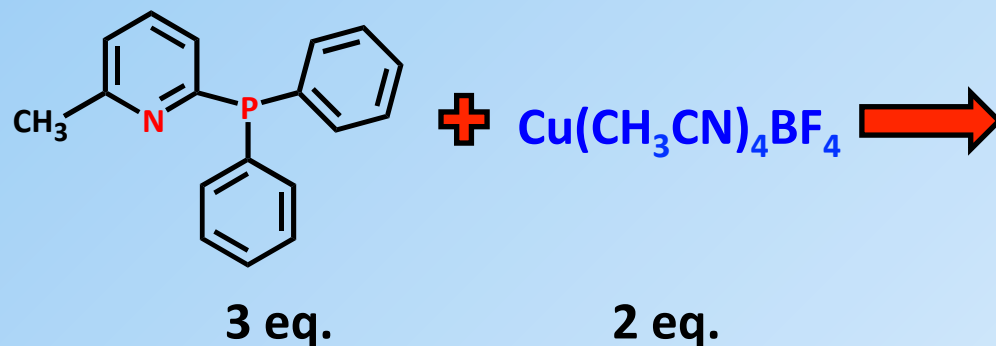
d¹⁰ complexes

A. Barbieri, G. Accorsi, N. Armaroli *Chem. Commun.* **2008**, 2185-2193 (Feature Article)

Color tuning with tetrahedral Cu(I) complexes

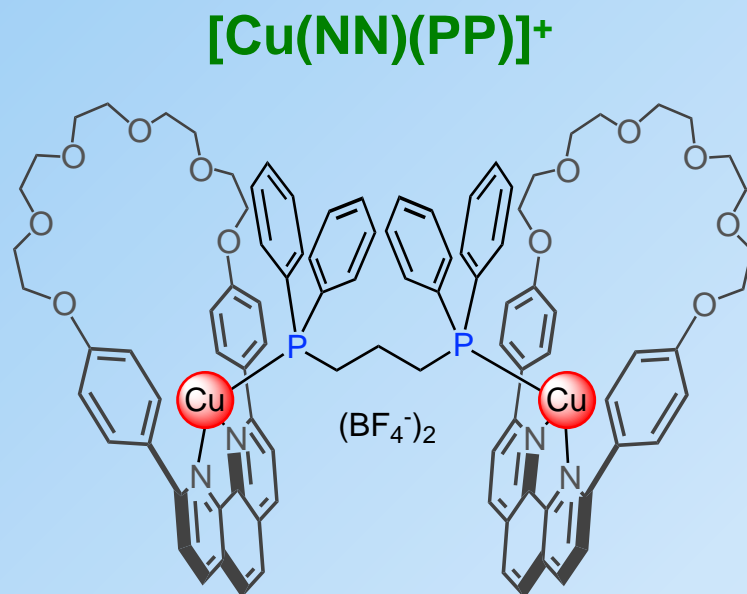


Recent example 1 - dinuclear cluster-like Cu(I) complexes



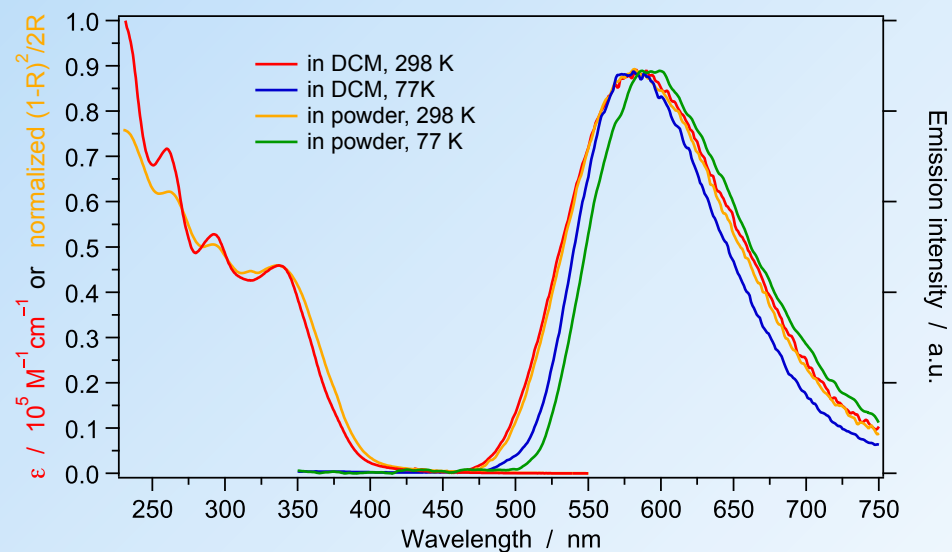
Chem. Commun. **2013**, 47, 859

Recent example 2 - dinuclear pseudorotaxane Cu(I) complexes

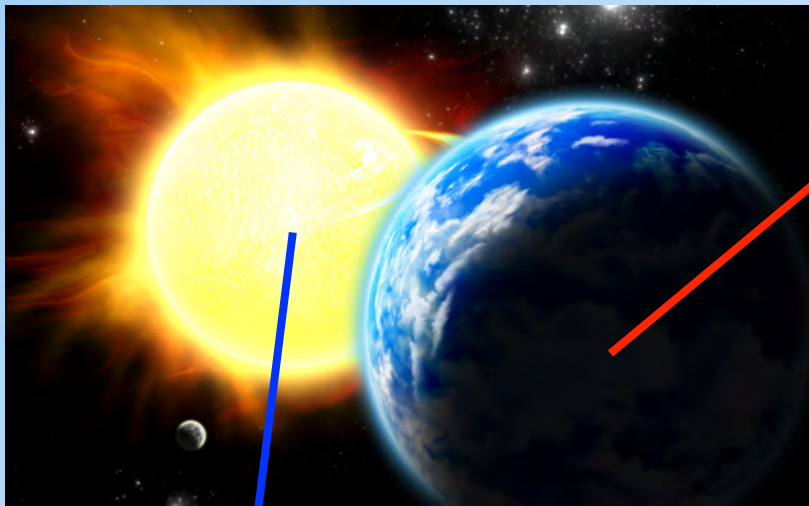


TRIGONAL GEOMETRY

Chem. Eur. J. **2014**, *20*, 12083



PERENNIAL ENERGY IS OVERABUNDANT ...
... AND HUMAN INGENUITY TOO ...
... BUT RESOURCES OF PLANET EARTH ARE LIMITED



**"EXTRATERRESTRIAL" INPUT
AMOUNTING TO THOUSANDS
OF TIMES OUR NEEDS**

**THE CONVERTERS OF SOLAR ENERGY ARE
MADE OF "TERRESTRIAL" MATERIALS,
HENCE THEY ARE AVAILABLE IN LIMITED
AMOUNTS**



RARE ELEMENTS IN ENERGY TECHNOLOGIES:

Some examples



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



**Neodymium, Praseodymium,
Dysprosium**

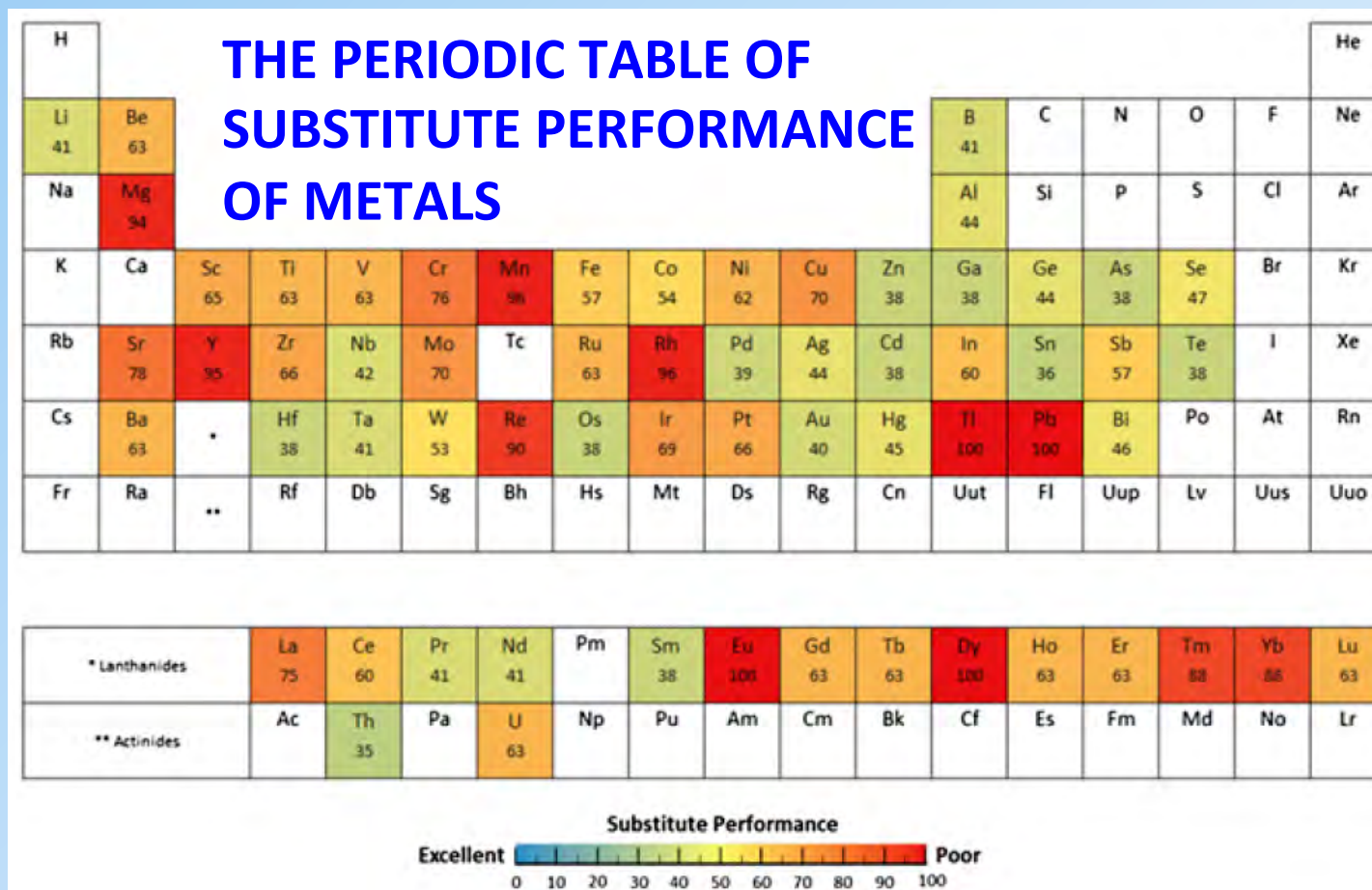


- Neodymium, Praseodymium
Dysprosium
- Lanthanum, Cerium; Lithium



**Europium, Terbium,
Yttrium, Cerium**

REPLACEMENT IS OFTEN NOT POSSIBLE (YET)

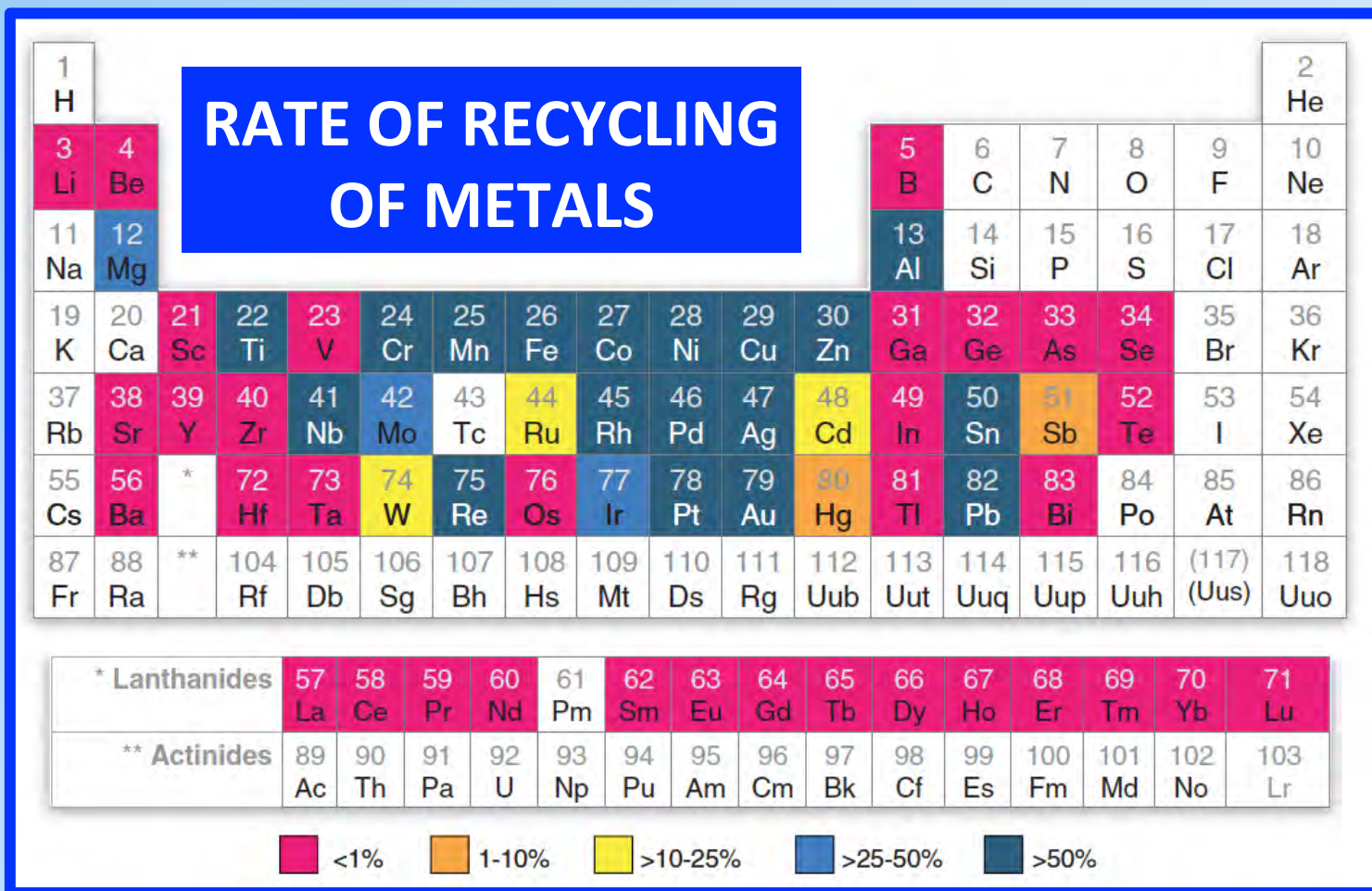


0 : exemplary substitutes exist for all major uses

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

Graedel et al. *PNAS* , DOI: 10.1073/pnas.1312752110

THE ONLY SOLUTION: RECYCLING



Science
2012, 337, 690

PRESENT RECYCLING RATES ARE TOTALLY UNACCEPTABLE

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EU: RESERVES OF CONVENTIONAL ENERGIES

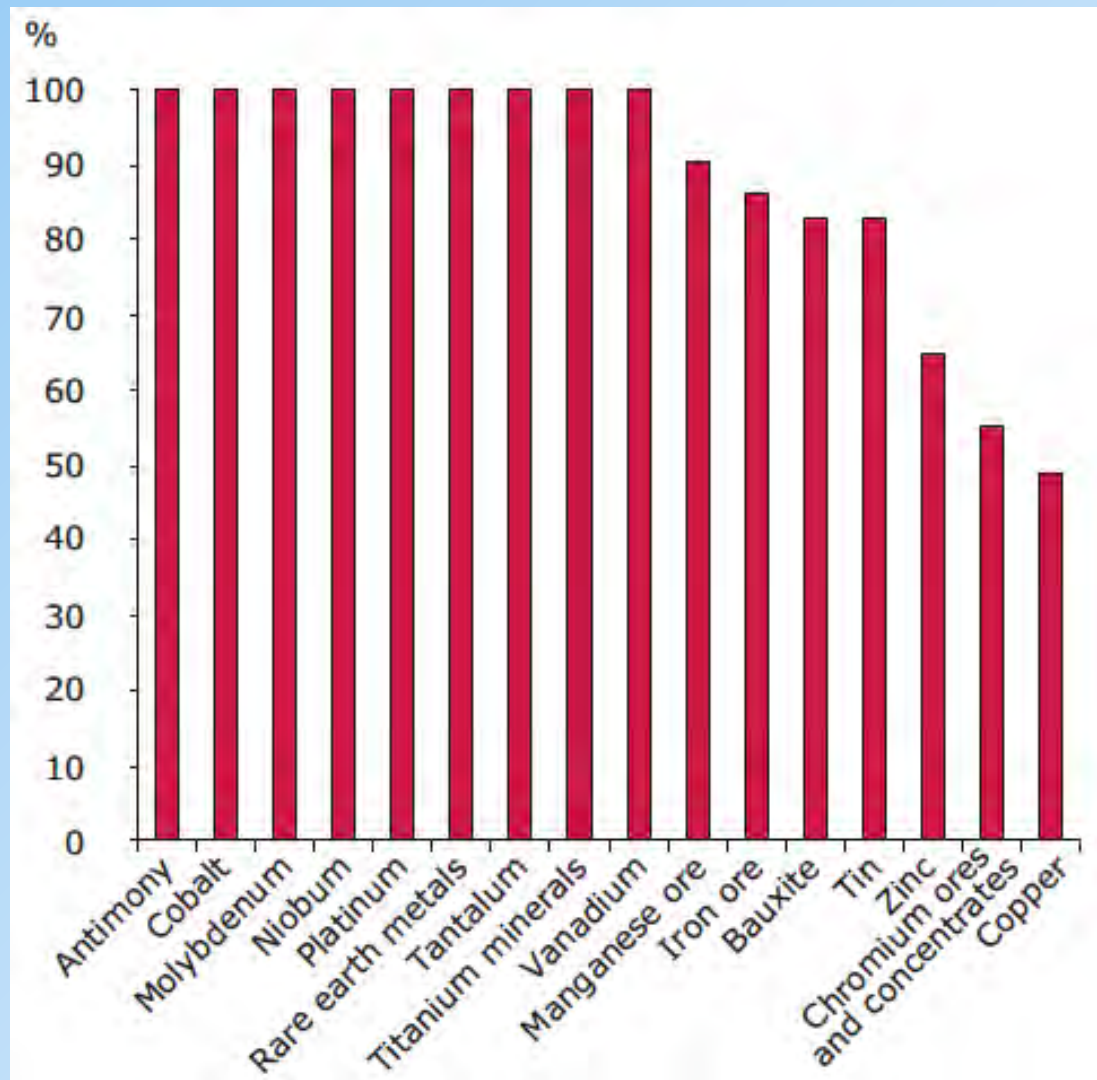
We own only **0.4, 0.8, 6.1 %** of the world's proved reserves of **oil, gas** and **coal** and we have virtually **no uranium** reserves*



We enjoy the best quality of life on Earth BUT our enviable prosperity is based on energy resources coming **FROM OTHER CONTINENTS**

*BP Statistical Review of World Energy, **2014**

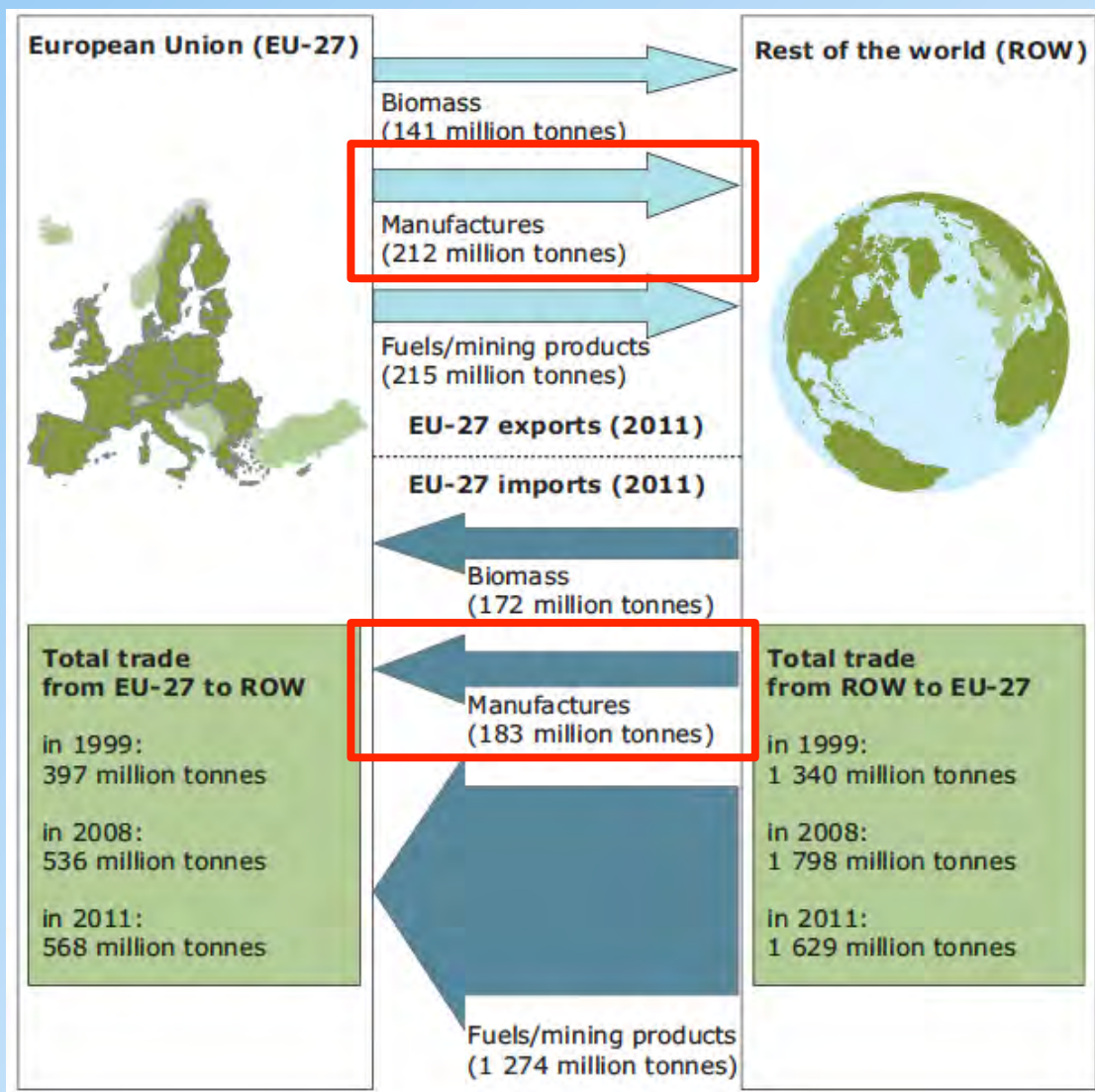
EU-27 : IMPORT OF METALS



**WE ALMOST TOTALLY
DEPEND ON IMPORTS**

Material Resources and Waste – Update 2012, EEA 2012

EU: IMPORT-EXPORT OF MATERIALS



**WE HAVE STILL
AN ADVANTAGE
ON HIGH ADDED VALUE
MANUFACTURING**

Material Resources and Waste – Update 2012, EEA 2012

FOSSILS vs. RENEWABLES: THE KEY DIFFERENCE

FOSSIL FUELS



THEY ARE “STUFF”
Either you have or
you don't have

RENEWABLE ENERGY TECHNOLOGIES



**THEY ARE MANUFACTURING
AND KNOWLEDGE**

WHERE WE SHOULD (POSSIBLY) GO

Increase public awareness: we are facing the toughest and most uncertain challenge ever faced by mankind

Abandon fossil fuels before they will abandon us

Stop the suicidal policy of cutting fund to education and research

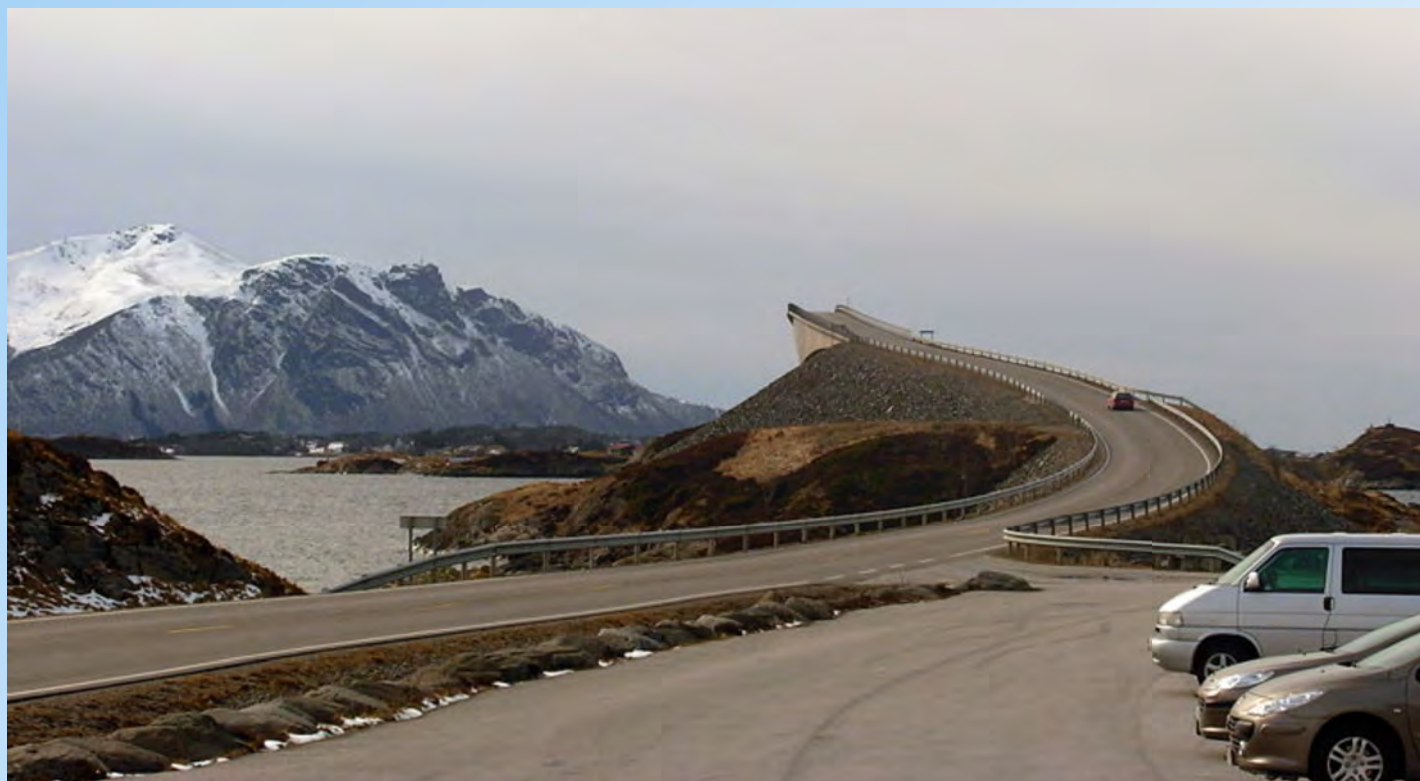
Favour the energy transition with adequate legislation

Stop weakening the commitment to decarbonization (as done recently ...)

Realize that energy transition is a huge opportunity , perhaps the only opportunity to save the EU economy

CONVENTIONAL RECIPIES TO REVIVE OUR ECONOMY HAVE FAILED FOR YEARS
WE ENTERED A NEW HISTORICAL PHASE
THE FOSSIL FUEL AGE IS IN ITS FINAL STAGE

WHAT IS DESPERATELY MISSING: A bridge between scientists and decision makers



WE ARE IN A HURRY

Without a bridge between knowledge and decision
THE ENERGY, CLIMATE AND RESOURCE CRISES CAN OVERWHELM US

THE ENERGY TRANSITION: CHALLENGES AND SOLUTIONS

CHALLENGES

Perennial energy sources

Energy efficiency

Energy convers. & storage

Critical materials

...

SOLUTIONS

Artificial Photosynthesis, ...

New Materials (e.g. for lighting)

Batteries, Fuel cells, Hydrogen

Recycling, Replacement

...

CHEMISTRY

BUT LET'S NOT LOOSE THE SENSE OF OUR LIMITS



Cleaning operations on the Louisiana coasts (USA), after the disaster of the Deepwater Horizon oil spill

Science & Technology are NOT the solutions to all of our problems

THE ENERGY TIMELINE

TIME FOR ACTION IS NOW

**Being up here
we have a huge
RESPONSIBILITY**

