

# *Earth, Environment and Energy*

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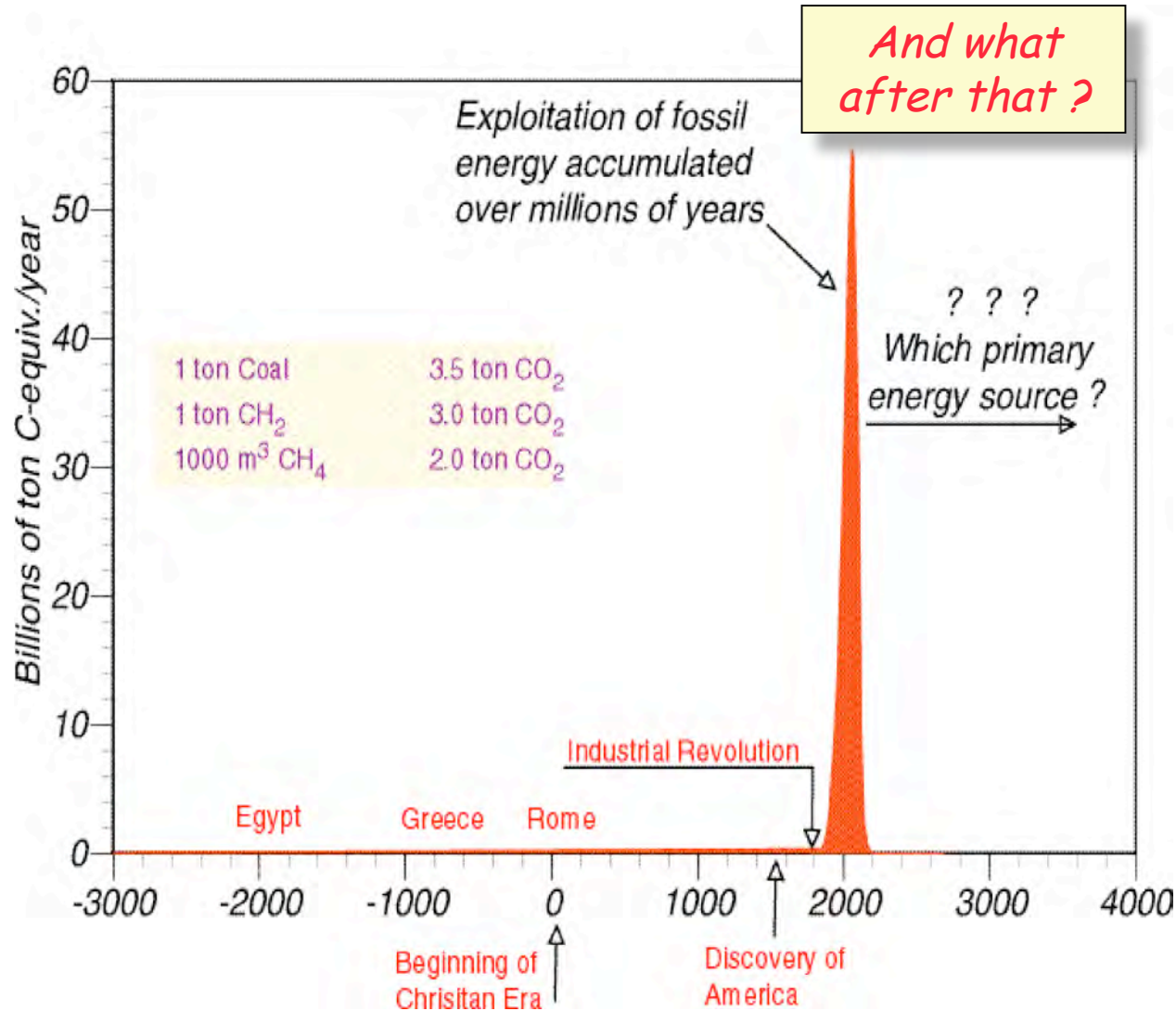
CERN, Geneva, Switzerland

CIEMAT, Madrid, Spain

# Summary

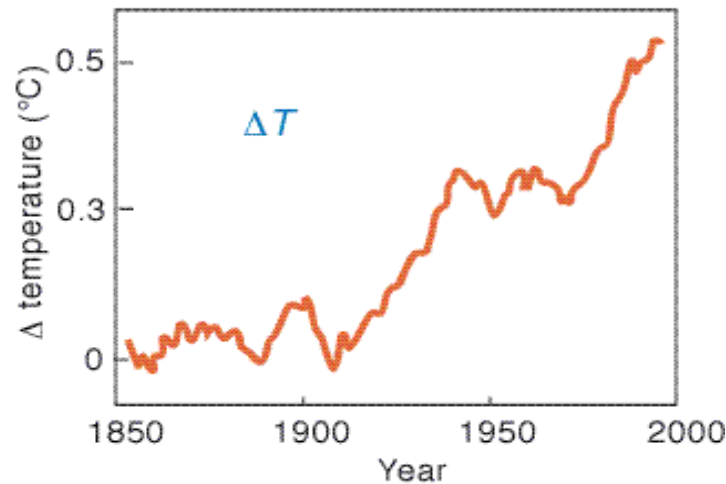
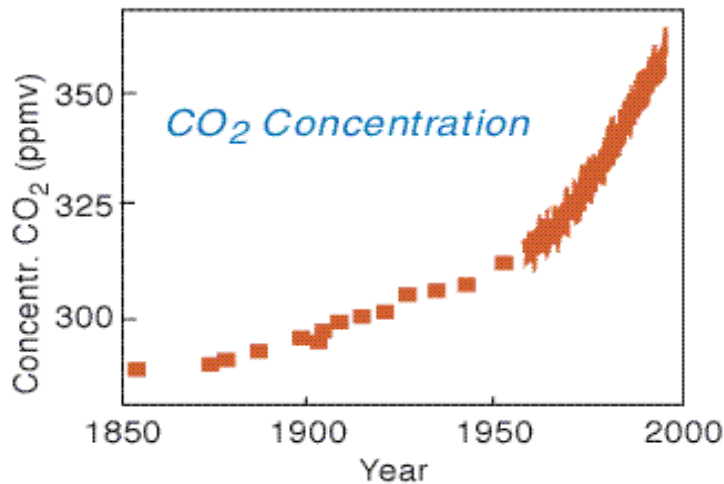
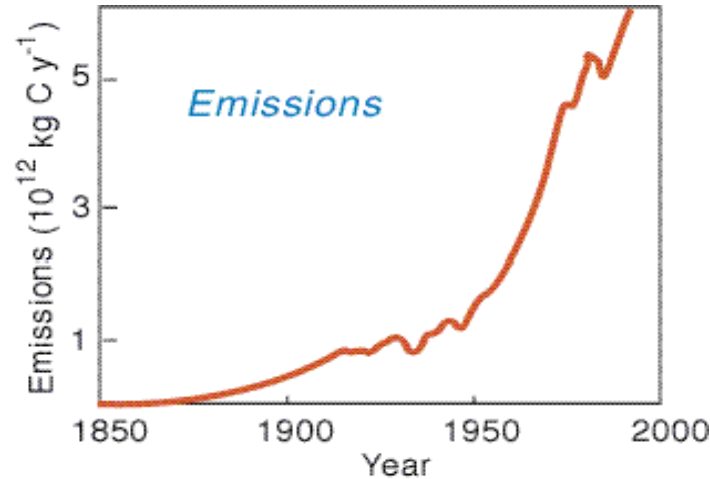
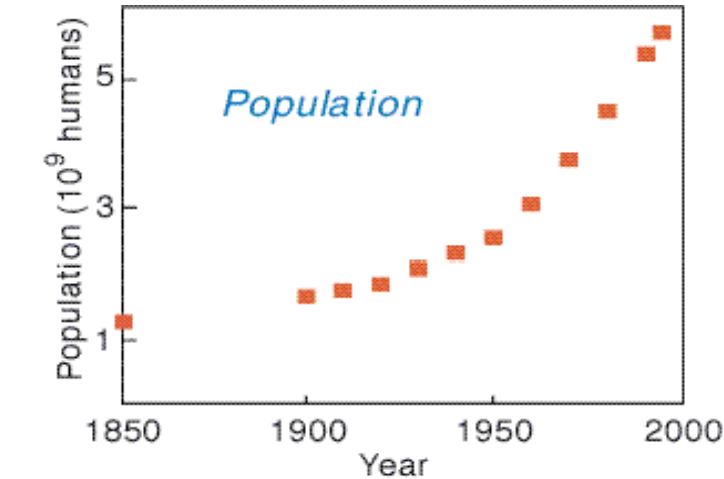
1. Population explosion and the demographic transition.
2. The long range consequences of growing CO<sub>2</sub> emissions.
3. Geo-engineering: reconciling fossils and climate ?
4. Clean Coal Sequestration (CCS) : a reality or an illusion ?
5. (Fast) conversion of CO<sub>2</sub> into carbonates ?
6. A "new economy" as a substitute to Oil ? Novel options:
  - I. Fossil hydrogen from NG with no CO<sub>2</sub> emissions
  - II. Hydrogen production from concentrated solar energy.
7. Hydrogen conversion to liquid fuels with the addition of previously sequestered CO<sub>2</sub>
8. A "dream": recovering CO<sub>2</sub> from the atmosphere.

# Energy and future



- At the present consumption level, known reserves for **coal**, **oil**, **gas** and **nuclear** correspond to a duration of the order of **230**, **45**, **63** and **54** years.
- The **longevity of the survival of the necessarily limited fossil's era** will be affected on the one hand by the discovery of new, exploitable resources, and on the other by the inevitable growth of the world's population and their standard of living.
- Taking into account the long lead time for the massive development of some new energy sources, **the end of the fossil era may be at sight.**

# Effects of human activities on the planet



- (1) Population
  - (2) Emissions
  - (3) Concentrations
  - (4) Climatic change
- **all correlated**

The exploitation of the the necessarily limited fossil era may be greatly shortened by the effects of global warming

# Upsala Glacier, Patagonia

1928



2004



# The population "explosion" and the Demographic Transition

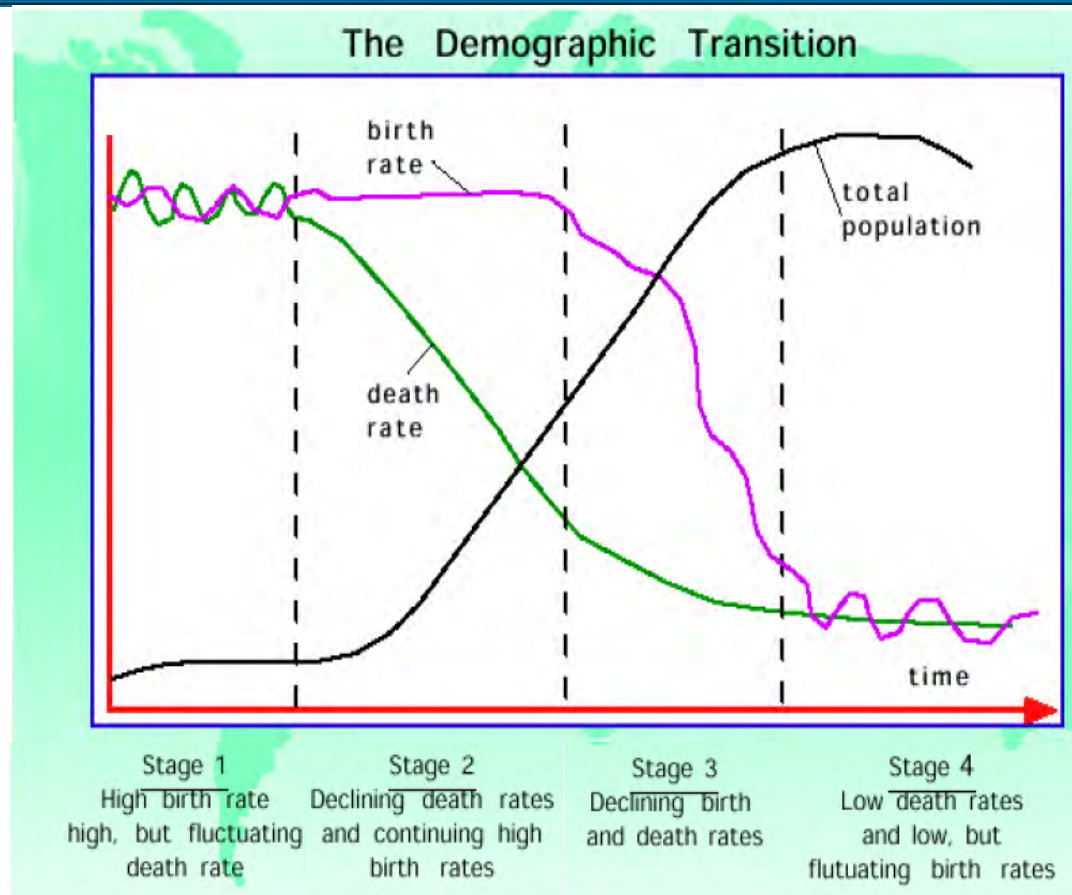


- Every second, 21 people are born and 18 die, a net gain of 3 people/s. Every day the population increases by 0.22 million people. The growth rate has been incessantly rising and it is currently approaching 90 million/year, with the rapid blowup of a **population explosion**.
- Such an immense growth of the human species is one of the most extraordinary evolutions of the planet Earth and no doubt it is conditioning the future of man as well as the one of any other animal and vegetal species.
- Within the 4300 millions of years of the life of the solar system, the "homo sapiens", its speech, language and fire all go back to far less than one million years from today.
- The total number of individuals which have ever lived on earth is estimated between 70 and 150 billions. Because of the exponential growth, **as many as 6 to 10 % of all human beings which have populated the earth are alive today.**

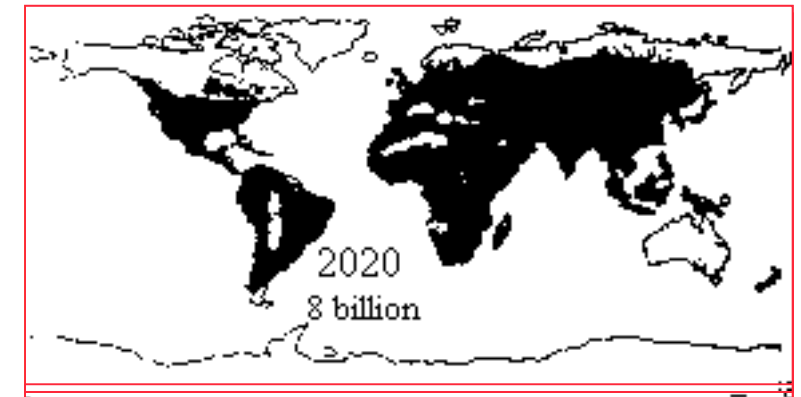
- Such an expanding population demands more and more food and energy, requires a greater consumption of mineral resources and exerts increasing pressure on the environment.
- This phenomenon occurs in every population and it is characterized by
  - ➡ A progressive reduction of the death's rate, followed by
  - ➡ a rapid decrease of the growth, followed by stabilization.
- This transition has occurred in all developed countries and it is currently happening on a global scale. It is accompanied by a general increase in economic growth and urbanization. The population begins to age — the elderly outnumber the young.
- Discovered in France on 18th century, the transition in the case of the modern interconnected world will presumably end within the 21st century.



# The population explosion



*1 2020; 8 billion*



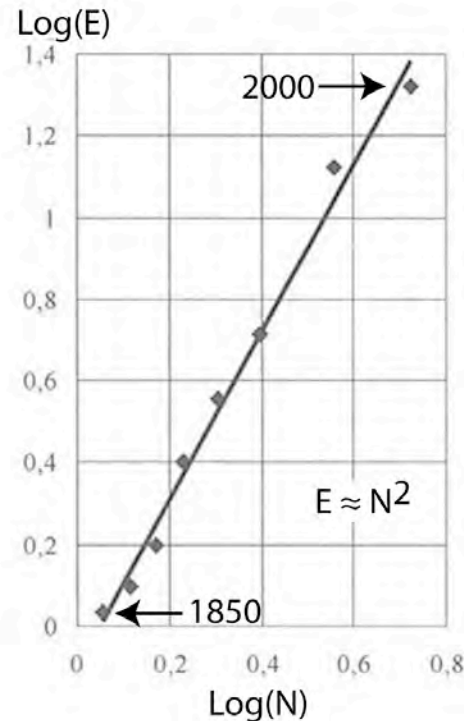
An "explosive" population growth: 90 M/year

Everybody will agree on the fact that future progress of mankind will be impossible without a very substantial amount of available energy, namely

*"New Energies are necessary to preserve long range future of Mankind"*

- At the beginning of the 19th century (population :  $10^9$ ) the average power was about 1kW/p, about 1/2 of a HP, 10 x his own human power.

- Since 1850, energy has grown twice as fast as population, i.e.  $E \propto N^2$ .

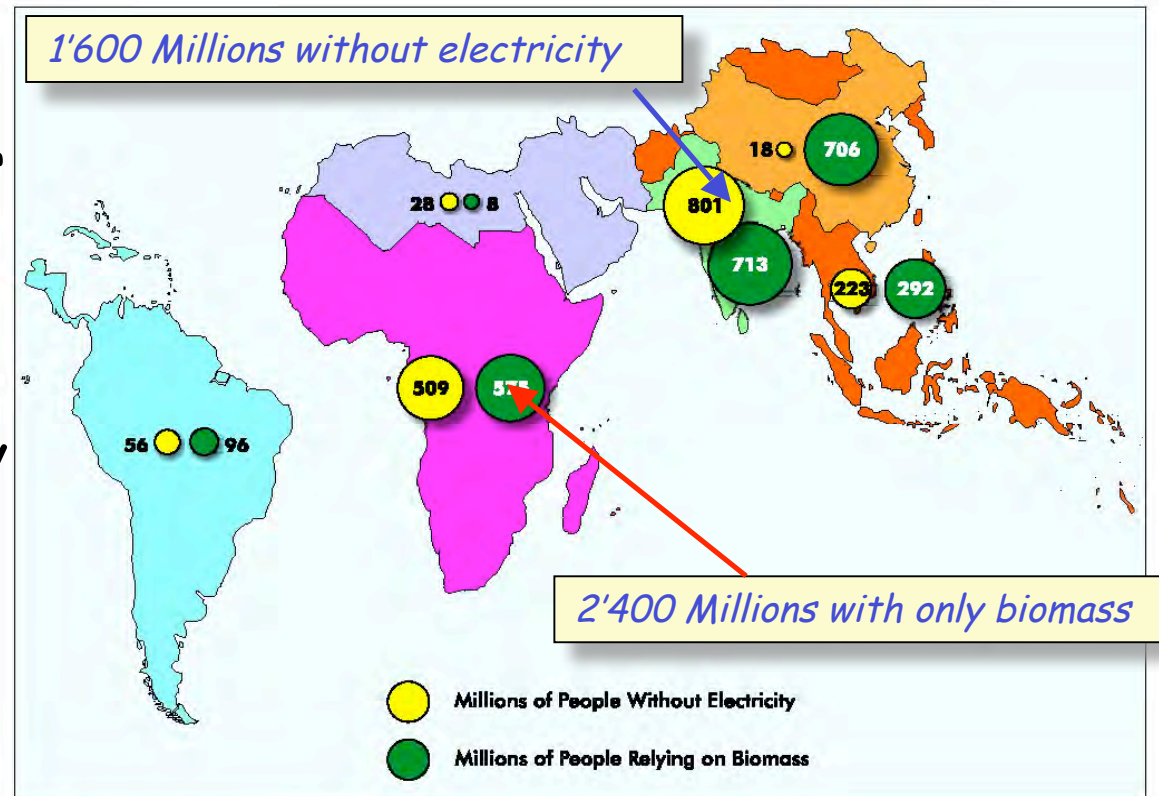


Year	Population Billions	Energy TWatts·Year
1850	1.13	0.68
1870	1.3	0.79
1890	1.49	1.0
1910	1.70	1.60
1930	2.02	2.28
1950	2.51	3.26
1970	3.62	8.36
1992	5.32	13.3
2000	6.10	14.5
2020	7.32	20.9
2050	10.05	39.4

- During the last 79 years, the global population grew by 3.42 times and the energy production increased 11.7 times.
- In 2000 mankind consumed 14.5 Twatt x year, a pro capite equivalent to 2.3 ton of coal, of the same order of the pro-capita nuclear weapons or of the energy required to launch each human being into space. For the US  $\approx 14$  t/y/p.

# Energy and poverty

- A huge correlation between lack of energy and poverty
- **1.6 billion** people - a quarter of the current world's population - are without electricity,
- About **2.4 billion** people rely almost exclusively on traditional biomass as their principal energy source.
- Of the 6 billion people, about one half live in poverty and at least one fifth are severely undernourished. The rest live in comparative comfort and health.



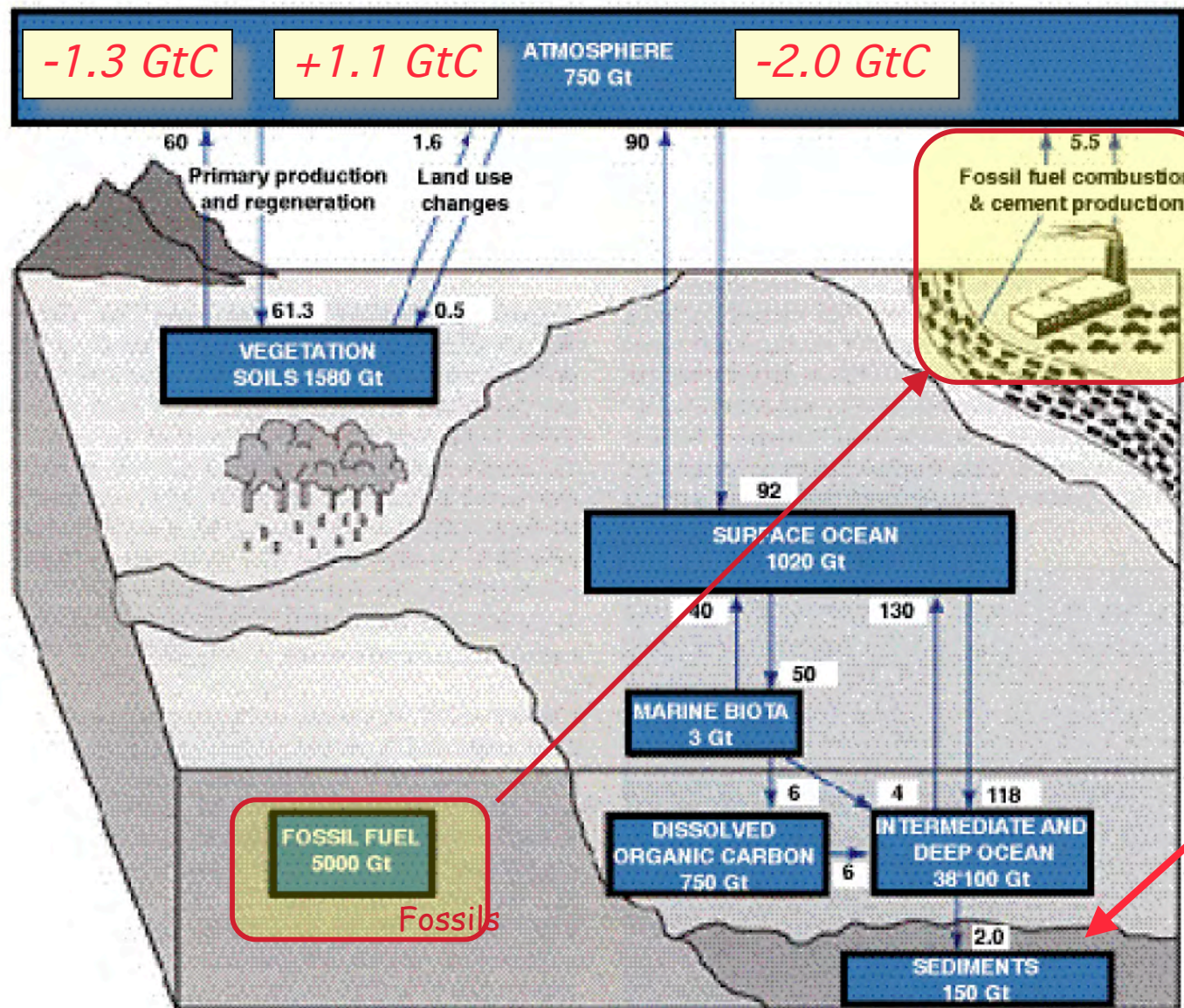
Source: IEA analysis.

*Technologically advanced countries have the responsibility of showing the way to the most needy ones !*

# The long range consequences of the growing CO<sub>2</sub> emissions



# Where is CO<sub>2</sub> going ?



1 ppmv CO<sub>2</sub> = 2.1 GtC

Antropogenic effects

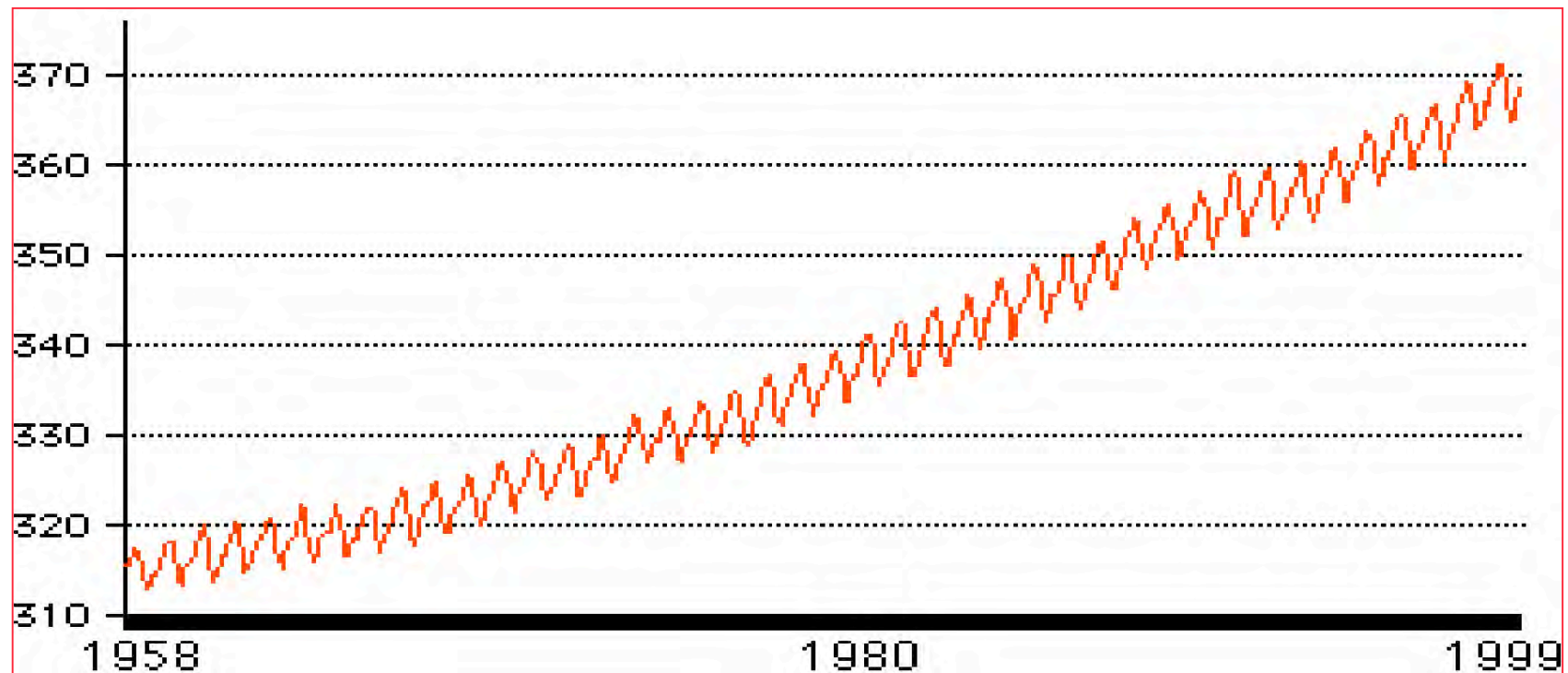
Ultimately most of the CO<sub>2</sub> excess will have to be carbonized in the deep oceans

2.0 GtC into Carbonates

Adapted from Climate Change 1994, published by the IPCC

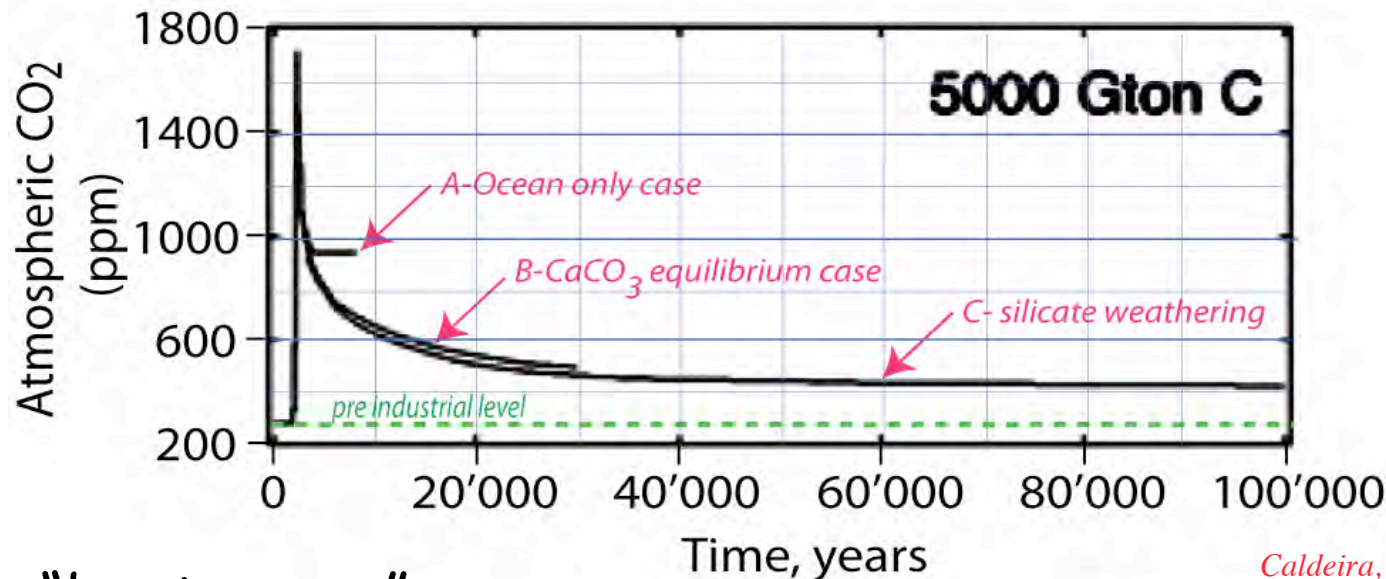
# CO2 emissions

CO2 concentration (in parts per million ppmv) of the air at the summit of Mauna Loa Hawaii, from 1958 to 2000





# How long will CO<sub>2</sub> last in the biosphere ?



- For the "best guess" case :
  - ➡ After 1'000 years 17-33% of fossil C
  - ➡ At 10'000 years 10-15% of fossil C
  - ➡ At 100'000 years 7% of fossil carbon
- The mean lifetime of fossil CO<sub>2</sub> is about 30-35 kyr
- Lifetime for public discussion might be "300 years, plus 25% that lasts forever."
- As a comparison, the lifetime of Pu-239 is 26 kyr, associated with the today's public perception of nuclear energy.

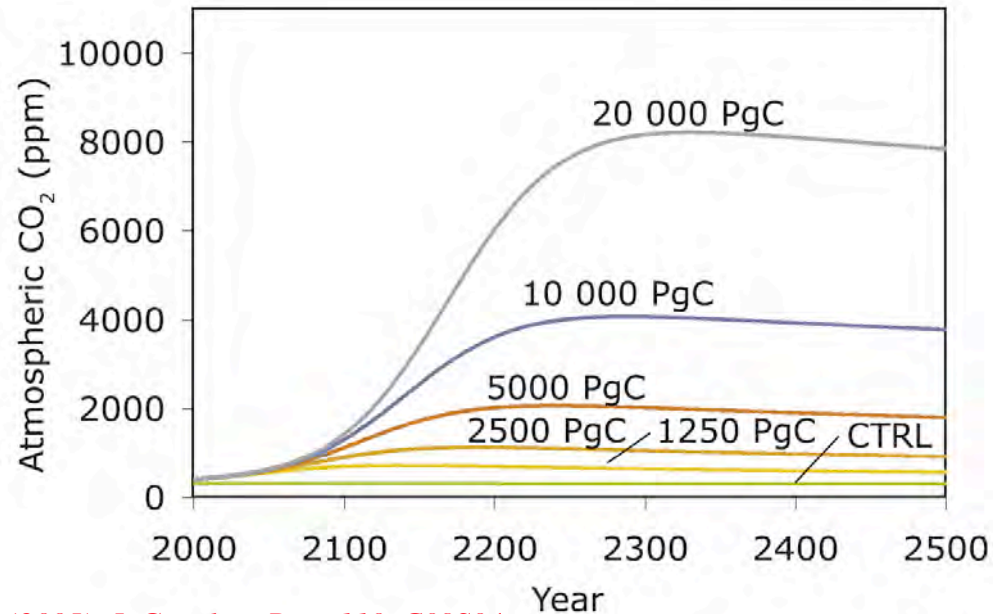
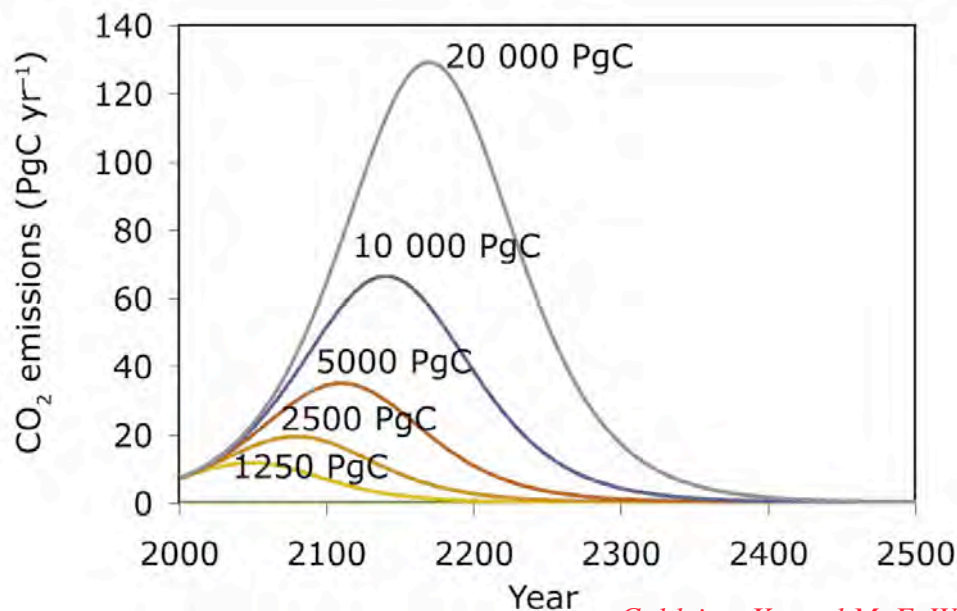
*Caldeira, K., and M. E. Wickett (2005), J. Geophys. Res., 110, C09S04.*

*Archer, D. (2005), J. Geophys. Res., 110, C09S05*



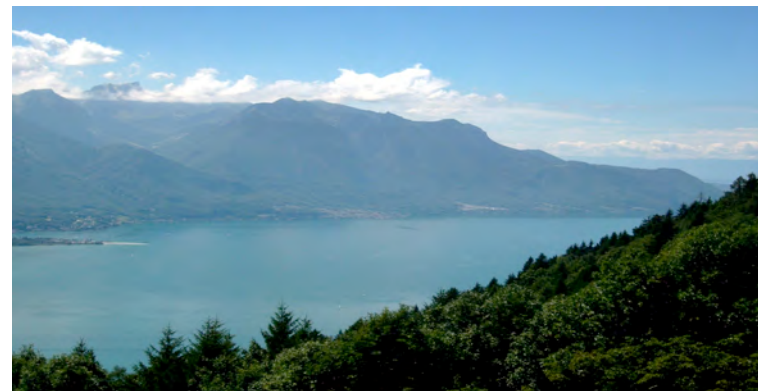
## Therefore...

- A mean atmospheric lifetime of order  $10^4$  years is in stark contrast with the "popular" perception of several hundred year lifetime for atmospheric  $\text{CO}_2$ .
- The 300 year simplification misses the immense longevity of the tail on the  $\text{CO}_2$  lifetime, and hence its interaction with major ice sheets, ocean methane clathrate deposits, and future glacial/interglacial cycles.



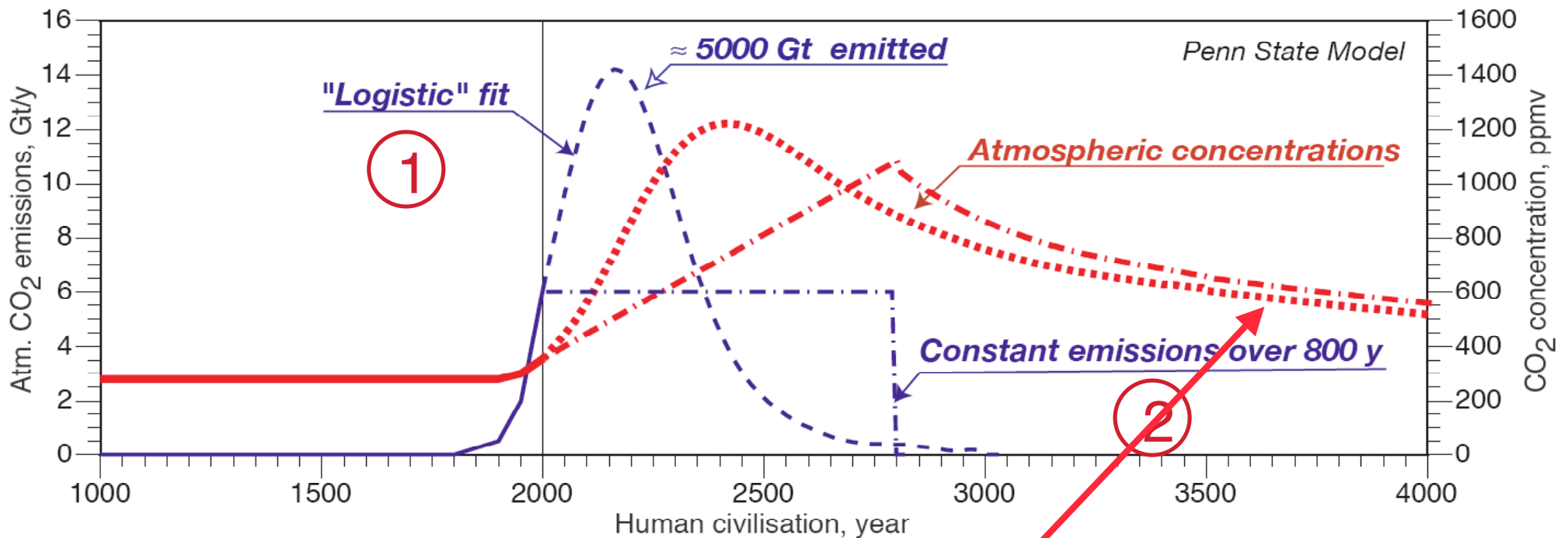
- Oil and Natural gas (about 500 Gton each) are expected to reach their limits sooner rather than later, due both to an increase of consumption and the progressive reduction of easily available resources.
- However there is plenty of cheap and readily available Coal. The known reserve is about 5000 Gton and it could be up to 20'000 Gton.
- Coal or Shales can be eventually converted to liquids (methanol or ethanol) to replace Oil and to gas (Syngas, Towngas and so on) to replace NG. but they require about twice as much CO<sub>2</sub> than Oil or gas.
- We recall as an example Germany during the last world war, with a massive use of gasoline from Coal in order to replace the wartime shortage of Oil.
- *There are sufficient amounts of Coal for half a millenium at twice the present level of (fossil) energy consumption.*

- Some of the world's biggest economies rely on coal. For instance, it provides almost 50% of USA's and Germany's electric power, 70% of India's and 80% of China's, a livelihood for billions of people, with a secure, domestic energy. But it produces twice the CO<sub>2</sub> of NG.
- Is there a way of reconciling fossils and climate ? Politicians' hopes are very high. The job is huge since already today about 20 billion tons of CO<sub>2</sub> are produced every year,
- At the present rate CO<sub>2</sub> is enough to fill with super-fluid CO<sub>2</sub> at >100 atm. the lake of Geneva (80 km<sup>3</sup>) every 4 years



# Assume that a major fraction of fossils are burnt....

- Technological improvements will, no doubt, will introduce other forms of energy: but the planet will continue notwithstanding to burn coal for a long time to come, *especially in those parts of the planet where the technological change is the slowest.*



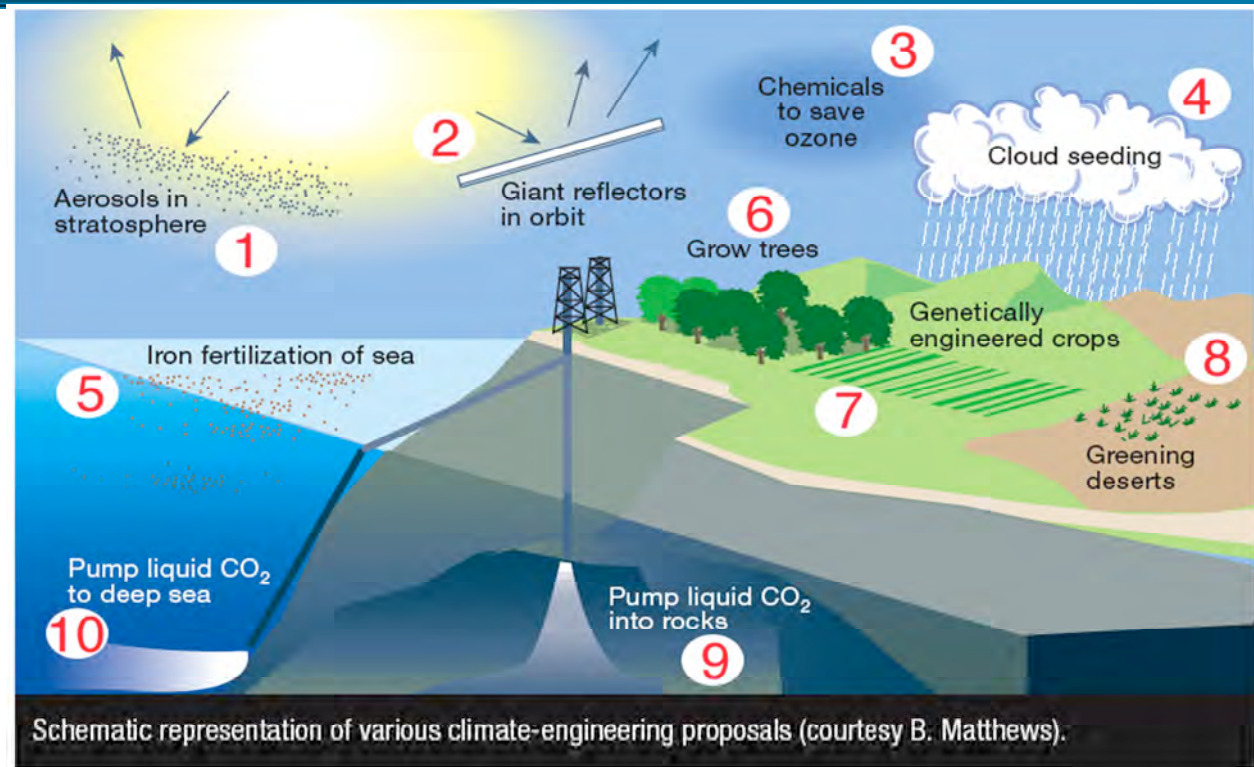
- Several millennia after today, the CO<sub>2</sub> concentration remains large and widely independent of the details of the process

# *Geo-engineering: reconciling fossils and climate*



# Geo-engineering for fossil CO<sub>2</sub> recovery ?

1. Aerosols in the stratosphere
2. Reflectors in orbit
3. Ozone preservation with chemicals
4. Cloud seeding
5. Iron fertilisation of sea
6. Grow trees
7. Genetically modified crops
8. Greening deserts
9. Pump liquid CO<sub>2</sub> into rocks
10. Pump liquid CO<sub>2</sub> to deep seas



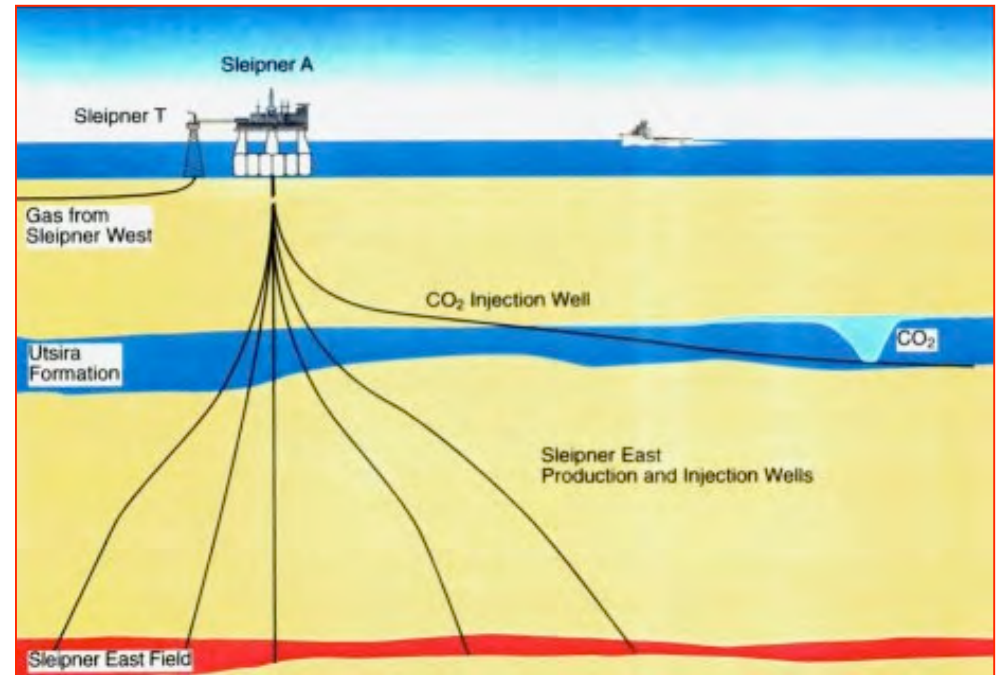
- Many of these ideas are unrealistic at the first sight, like for instance the proposal for huge reflectors in space (2)
- Notwithstanding they evidence the extreme difficulty in facing the consequences of growing fossil emissions.
- These considerations should foster a serious debate on maybe other, truly innovative ideas on the planetary scale.

# *Clean Coal Sequestration (CCS): a reality or an illusion ?*

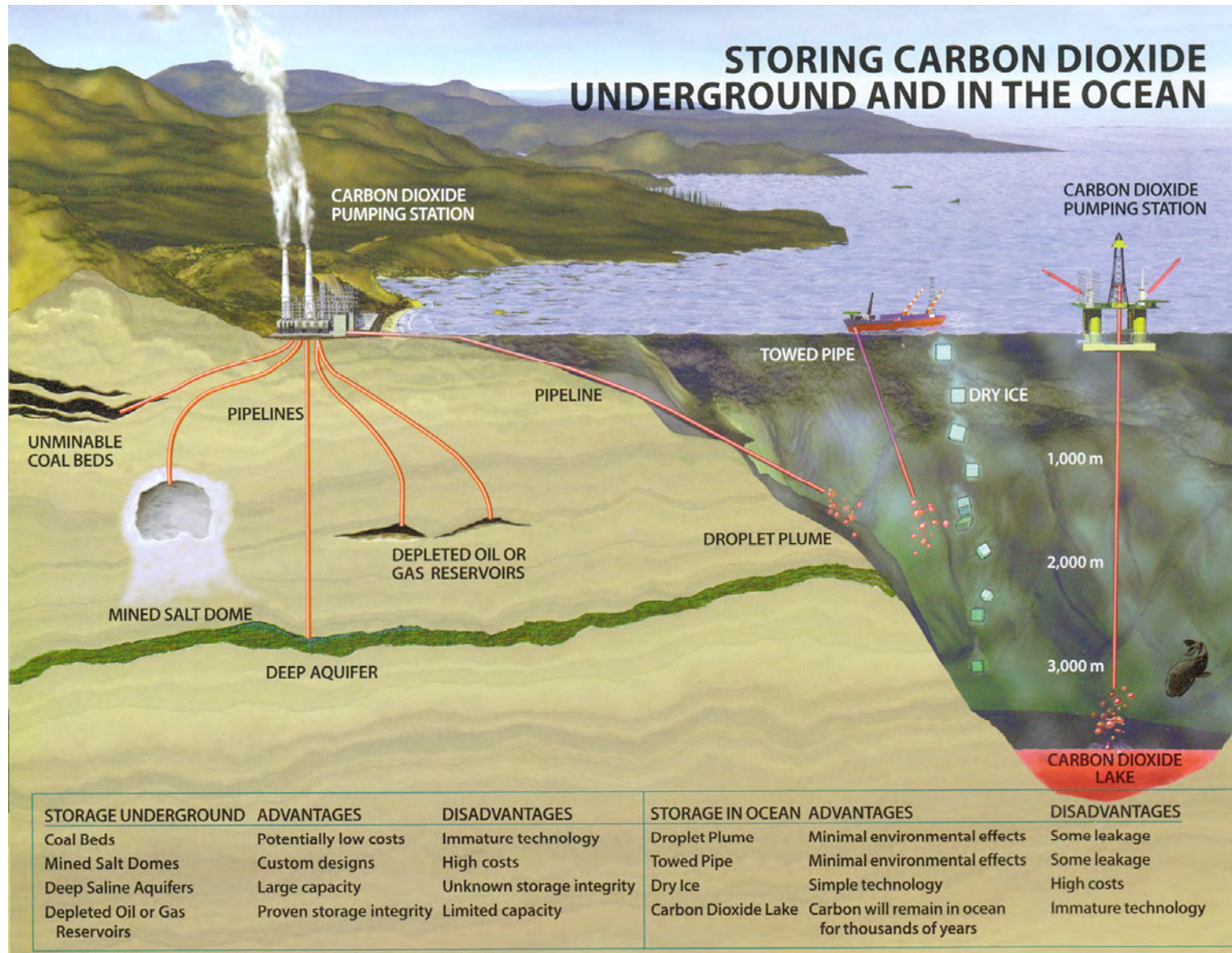


# Clean coal: a reality or an illusion ?

- **Sequestration (CCS)** is seriously considered: inject the CO<sub>2</sub> down into the earth or at the bottom of the ocean.
- Already used by the oil industry, but at the level of few million tons/y.
- Some \$3.4 Billion have been already spent by USA and similar incentives have been given by EECC and elsewhere.
- Many sources of CO<sub>2</sub> are not applicable to CCS.
- Sequestration is not elimination and eventually CO<sub>2</sub> will have to come back in the atmosphere, after dissipation of the greenhouse effect: thousand of years of accumulation !

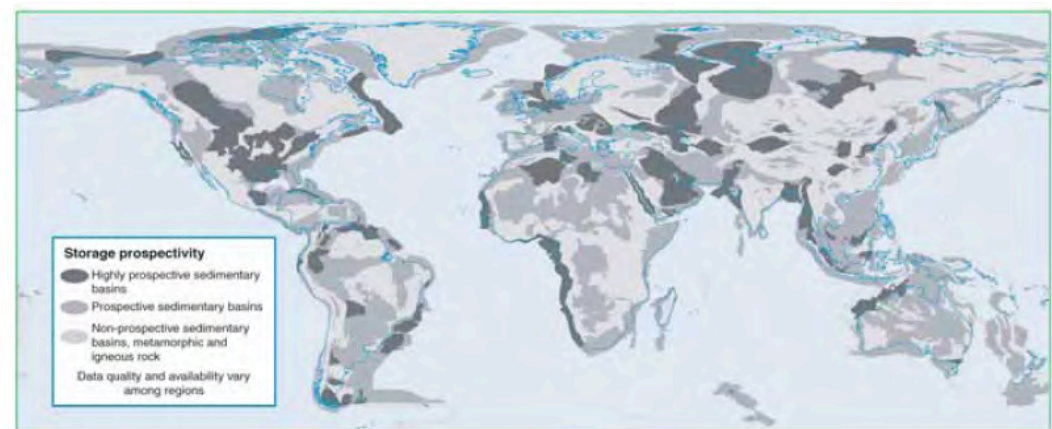
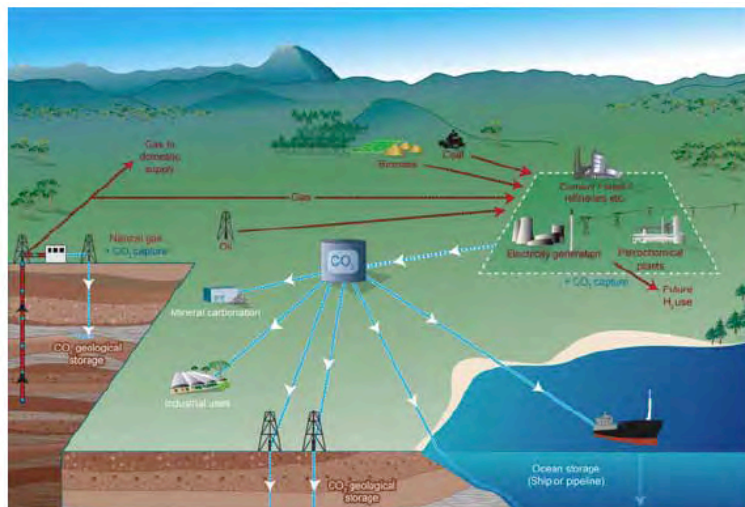
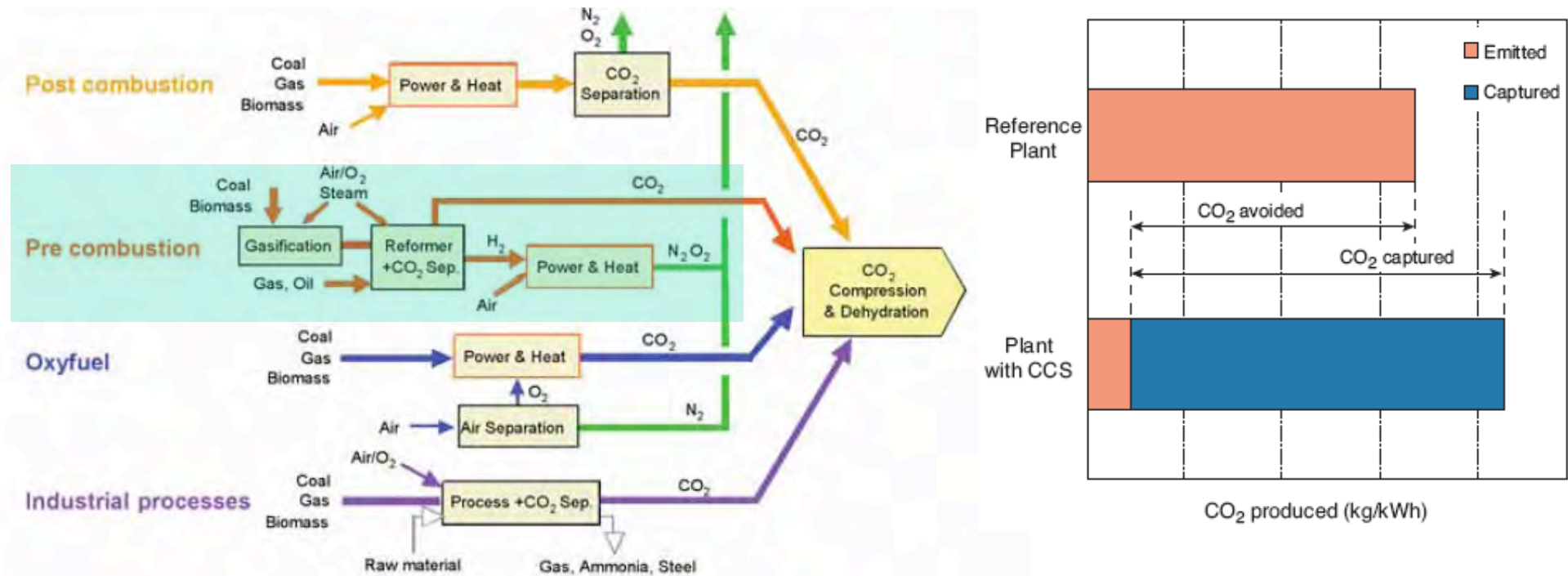


# : Storage sites for carbon dioxide [Herzog 2000]



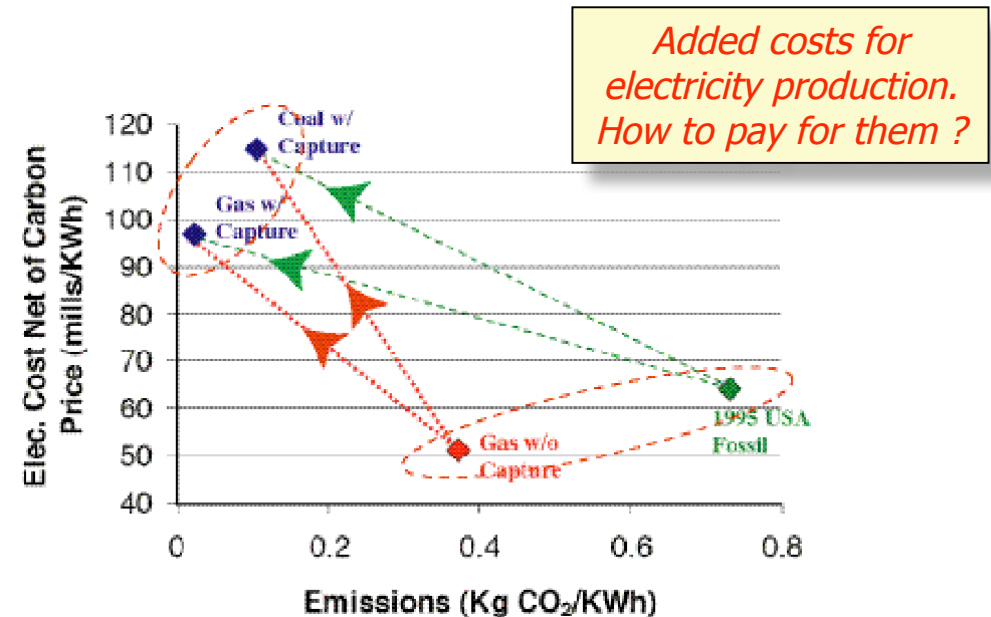
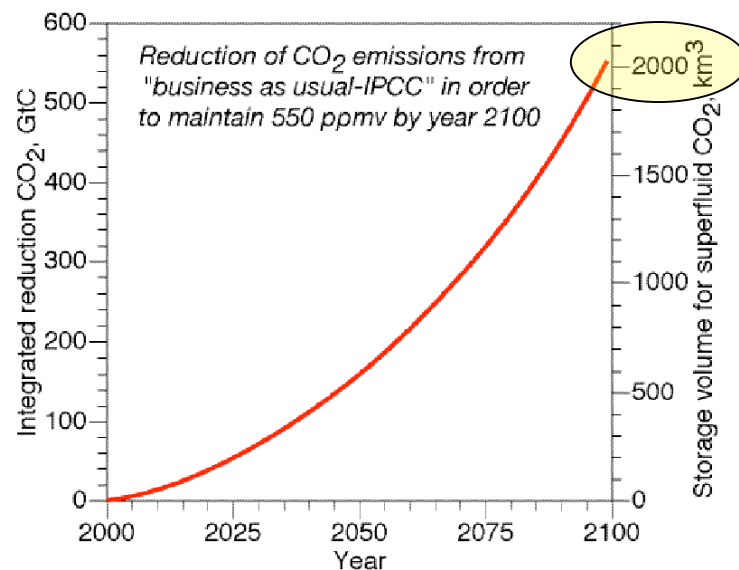


# Underground CO<sub>2</sub> sequestration: methods



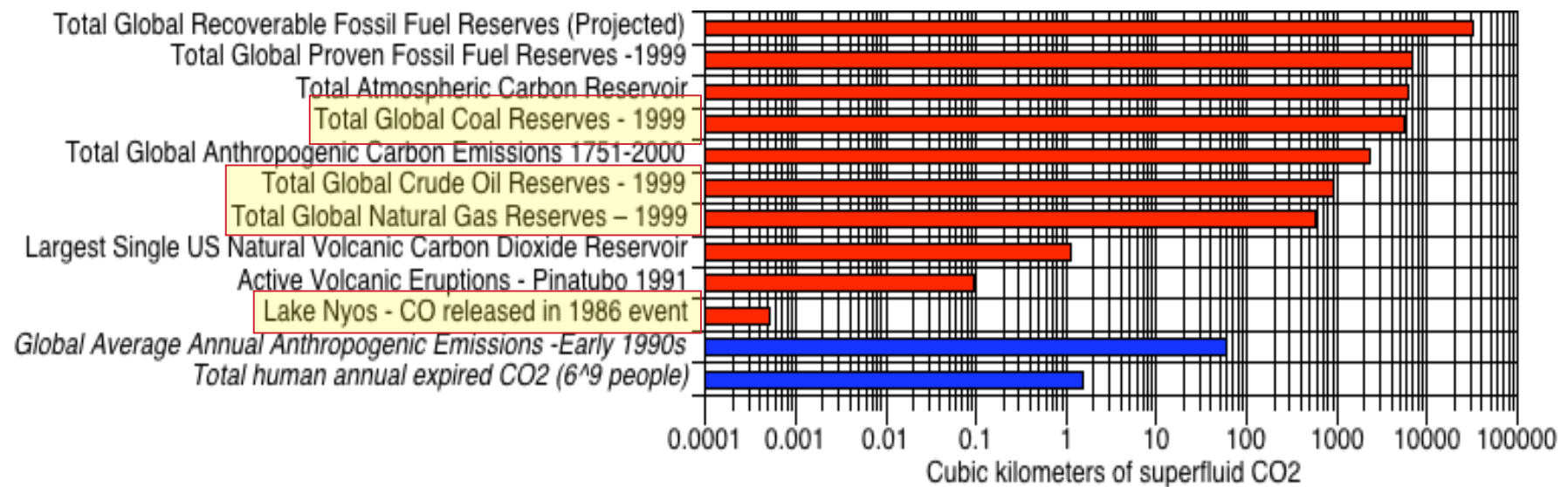
# Underground sequestration of CO<sub>2</sub> ?

- As ambient temperature, the CO<sub>2</sub> becomes liquid ( $d \approx 1,1$  kg/l) for pressures larger than 110 atm. It can therefore be injected at great depth ( $> 1\text{km}$ ) under land or under sea.
- In order to be effective, the quantities of CO<sub>2</sub> are enormous: in order to ensure by 2100 a level equal to twice the pre-industrial level (550 ppm) we must accumulate  $\approx 2000 \text{ km}^3$  of super-fluid CO<sub>2</sub>. Each km<sup>3</sup> contains  $1.1 \times 10^9$  tons.



# Environmental risks of CO<sub>2</sub> sequestration

- In addition to technological developments and added costs, the use of sequestration represents **very serious potential environmental risks**.
- Although not toxic, at concentrations above some %, CO<sub>2</sub> act as powerful brain vein dilatators. In a few minutes, unconsciousness occurs at 15 % of relative concentration and immediate death at 30%. In some cases death was observed already at 9%.
- In 1986, at lake Nyos a volcanic CO<sub>2</sub> leak of  $2.4 \times 10^5$  t has killed all 1746 people < 15 km from the source and < 24 hours after the event. Insects, animals, people in the invisible cloud dropped almost instantaneously unconscious, comatose or dead.



# Safety considerations

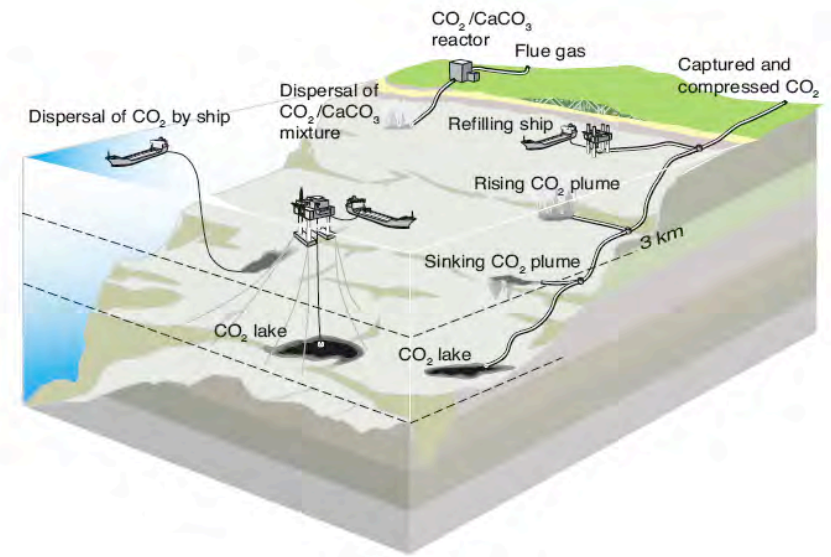
- The degradation processes for the sealed well and the reservoir behaviour over long timescales are very difficult to predict.
- On general grounds one may consider that the likelihood of leaks from a  $\text{CO}_2$  reservoir during the sequestration process should be similar to that of hydrocarbon reservoirs during production, with significant leaks ( $> 10 \text{ t/day}$ ) expected to be about  $10^{-3}$  per reservoir year.
- After the reservoir is sealed, after many centuries, the uncertainty about leak frequency is probably higher. Unlike abandoned hydrocarbon reservoirs, the  $\text{CO}_2$  reservoir will be under pressure.
- The expanded and denser  $\text{CO}_2$ , if promptly emitted, will be very cold and hence remain at the surface of the escaping area: it may represent a major risk for the nearby population.



# CO<sub>2</sub> ocean storage ?

- The injection of many hundreds of GtCO<sub>2</sub> will produce large changes in the region of injection and measurable changes over the whole ocean volume:

- ➡ 10% mitigation for 550 ppmv produces PH changes >0.4 over >1% ocean volume
- ➡ Adding CO<sub>2</sub> harms marine organisms: reduced calcification, reproduction growth, circulatory oxygen supply and increased mortality
- ➡ Immediate mortality is expected close to injection points or CO<sub>2</sub> lakes

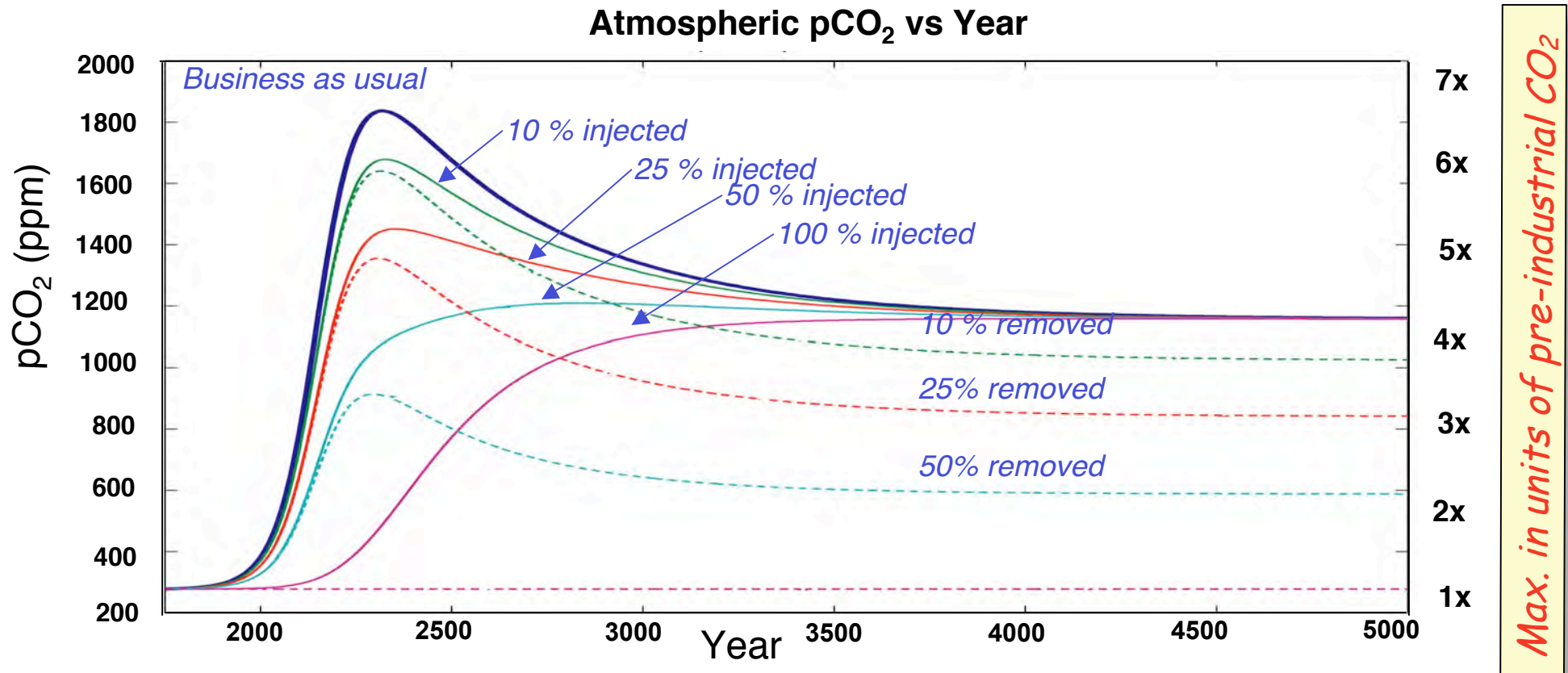


↓ Fraction of CO<sub>2</sub> surviving as function of depth and time

Year	Injection depth		
	800 m	1500 m	3000 m
2100	0.78 ± 0.06	0.91 ± 0.05	0.99 ± 0.01
2200	0.50 ± 0.06	0.74 ± 0.07	0.94 ± 0.06
2300	0.36 ± 0.06	0.60 ± 0.08	0.87 ± 0.10
2400	0.28 ± 0.07	0.49 ± 0.09	0.79 ± 0.12
2500	0.23 ± 0.07	0.42 ± 0.09	0.71 ± 0.14



# Sequestration is in the long run far less effective

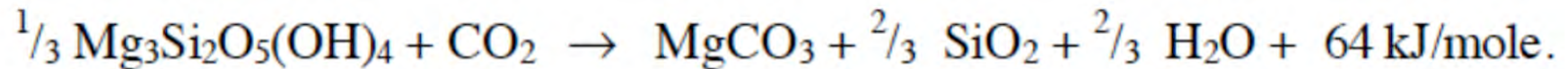


- Integrated effects of sequestration, even if performed most efficiently, are only postponing the emission pattern.
- Removal, with the help of novel technologies, is far more efficient.

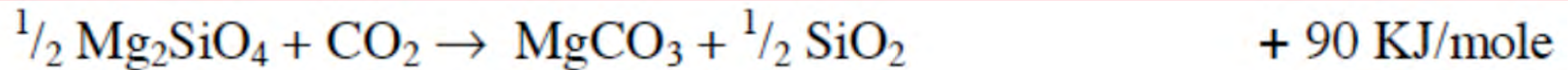
(Fast) conversion of  $\text{CO}_2$   
into carbonates ?

# Mineral carbonation

- Mineral sequestration involves the reaction of CO<sub>2</sub> with minerals to form geologically stable carbonates, i.e. mineral carbonation, with the potential to convert naturally occurring silicate minerals to geologically stable carbonate minerals and silica.
- This process emulates natural chemical transformations such as weathering of rocks to form carbonates. Some examples are
  - ➡ The common silicate mineral **serpentine**, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, and CO<sub>2</sub> into magnesite, MgCO<sub>3</sub>, silica and water. Using this ideal case, one ton of serpentine can dispose of approximately one-half ton of CO<sub>2</sub>.

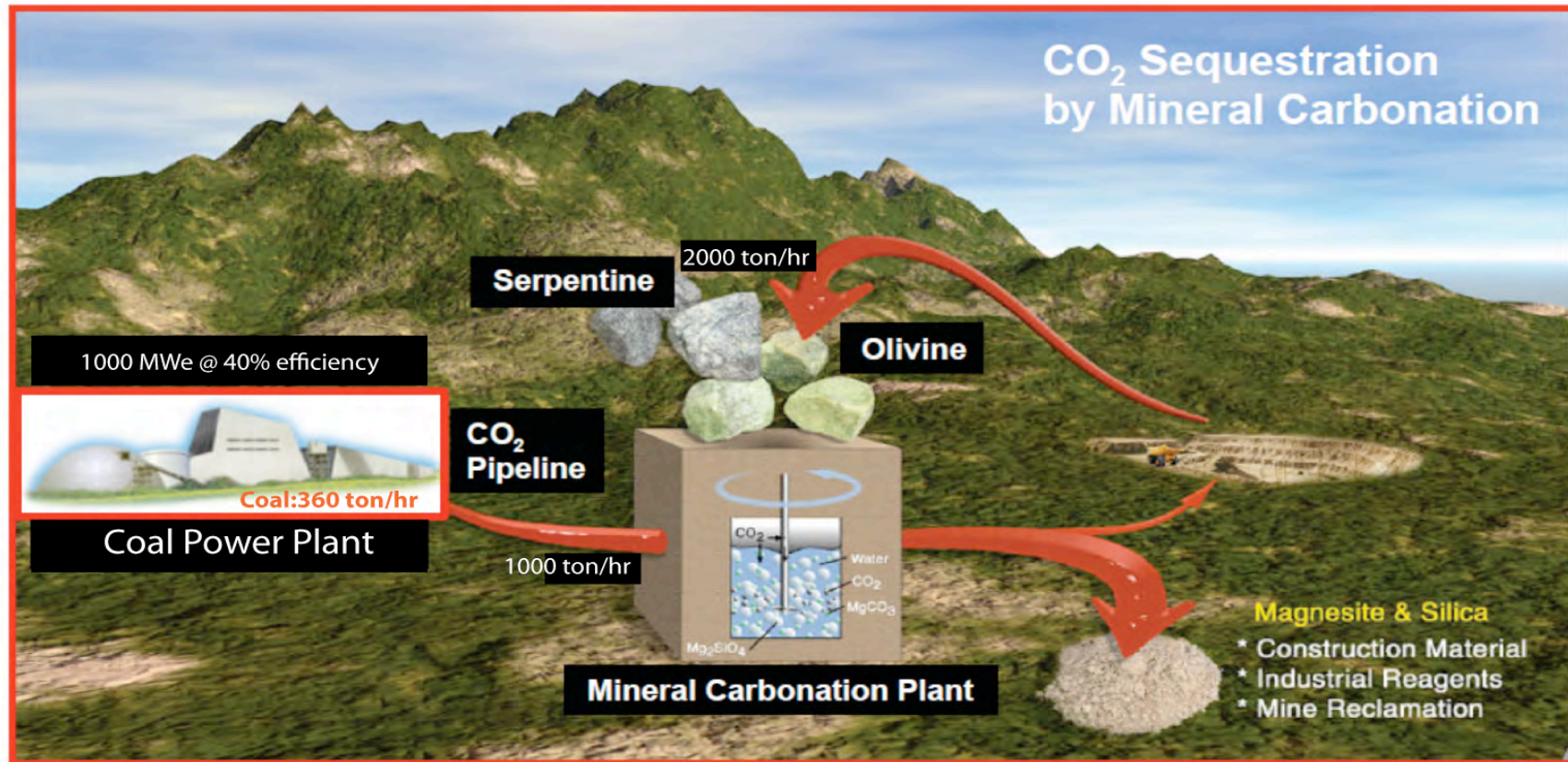


- ➡ The forsterite, which is the end member of the common silicate mineral **olivine**. One ton of olivine can dispose of about 2/3 of a ton of CO<sub>2</sub>. The reaction is exothermic and releases 90 KJ/mole of CO<sub>2</sub>.



- The minerals must be initially finely crushed to a dust of micron size. The long reaction time and demanding reaction conditions contribute to process expense. The amounts of minerals are very relevant, far heavier than the initial coal supply (almost an order of magnitude).

# Mineral carbonation



Courtesy of Albany Research Center

- We need new and demanding reaction conditions, namely
  - ⇒ faster reaction pathways
  - ⇒ the process has to be economically viable.
  - ⇒ it is generally very difficult to recover the low-grade heat.
  - ⇒ the environmental impact from mining + carbonation must be considered.



## In situ, “ sponge like” carbonation by rocks ?

- Kelemen and Matter have observed that in Oman natural carbonation of peridotite (olivine  $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$  and pyroxene  $[(\text{Ca},\text{Mg},\text{Fe})_2\text{Si}_2\text{O}_6]$ ), is surprisingly fast, with an average  $^{14}\text{C}$  age of 26,000 years, rather than 30-95 million years as previously believed. Data show that  $10^4$  to  $10^5$  tons/y of atmospheric  $\text{CO}_2$  are converted to carbonate.
- The idea is that Peridotite carbonation may be accelerated via drilling, hydraulic fracture, input of purified  $\text{CO}_2$  at elevated pressure, and increased temperature at depth.
- The carbon-rich superfluid  $\text{CO}_2$  reacts with peridotite, creating calcite and magnesite, and an exothermic reaction. As they fill the voids they expand, causing the peridotite to crack, and thereby creating more surface area for the  $\text{CO}_2$  to react with.
- The authors claim that because of the high density of  $\text{CO}_2$  and the exothermic reaction, the rate is up to  $10^6$  times faster than natural rates, potentially consuming billions of tons of atmospheric  $\text{CO}_2$  per year.
- Evidently this for the moment is only a simple idea and a large amount of work is needed before it may eventually become a reality.

# The hydrogen alternative ?



## A “Hydrogen ” economy ?

- Oil and NG are not only our main energy sources: they are also essential materials for a great variety of products (for example many petrochemical and chemical products including synthetic materials, plastics, pharmaceuticals, etc.).
- Given by nature as a gift, they are being used up rather rapidly and become significantly depleted and increasingly costly. **We need to search for new sources and solutions.**
- Much has been said about a future “hydrogen economy”. Hydrogen is indeed clean, giving only water and energy.
- Governments and some major industries seem to be committed to develop the “hydrogen economy” (see for example the statements by President Bush’s January 2003 State of the Union message and President Prodi’s talks at the EEUU).
- It is clear, however, that in order to achieve this, **new ways without CO<sub>2</sub> must be found to make it feasible.**

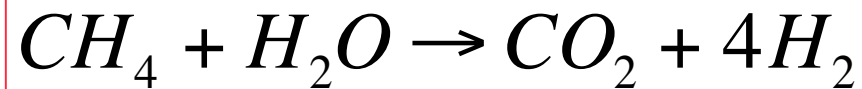
## Hydrogen is only an energy carrier

- However, hydrogen is not a natural energy source on our planet (in contrast to the sun and stars) and it may be presently generated for instance from natural gas or coal.
- Handling of this volatile and explosive gas is difficult, dangerous and costly, necessitating high pressure equipment and the use of special materials. No infrastructure exists for it and its costs, without a doubt, will be prohibitive.
- Even with the greatest care, any leaks would represent extreme explosion hazards, limiting wide use by consumers.
- The new sources of  $H_2$  must avoid the associated production of  $CO_2$  in the process, since its increase in the atmosphere is considered a major man made cause for global warming.

# Fossil hydrogen from NG with no CO<sub>2</sub> emissions

## NG to H2 transformation ?

- H2 production is  $1.9 \times 10^{11} \text{ Nm}^3/\text{y}$ , 17 Mton/y, energetically equivalent to  $\approx 5\%$  of the world oil production (84 MBOL/d)
- Steam methane reforming (SMR) is the most common and least expensive method of producing commercial H2 as well as in the industrial synthesis of ammonia ( $10^8 \text{ t/y}$ ) from H2.
- The process is undertaken mostly starting from NG with 700 - 1100 °C with energetic efficiencies of NG to H2 of 70 - 80%.



- The main inconvenience is the associated large CO2 production of  $29.25 \text{ kgCO}_2/\text{GJH}_2$ .
- An alternative with no CO2 emissions is the one in which NG is heated enough to split spontaneously NG into H2 + carbon.

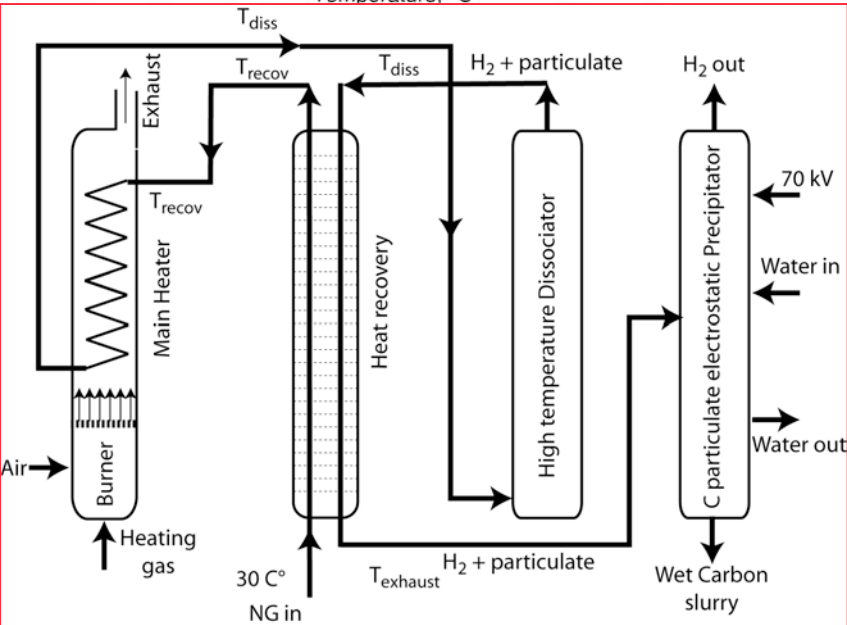
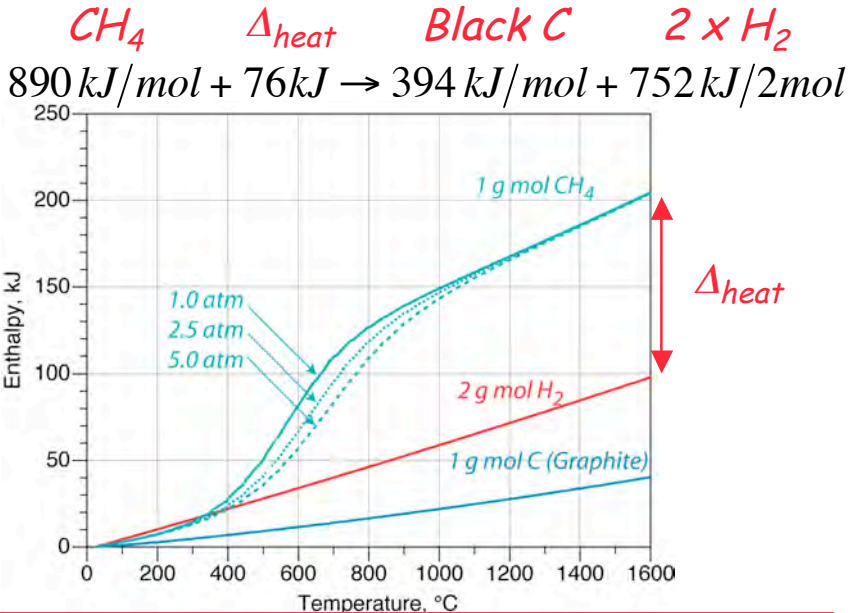


- *As a main result, the H2 yield for a given NG is halved*



## Principle of NG to H<sub>2</sub> dissociation with no CO<sub>2</sub> (CIEMAT)

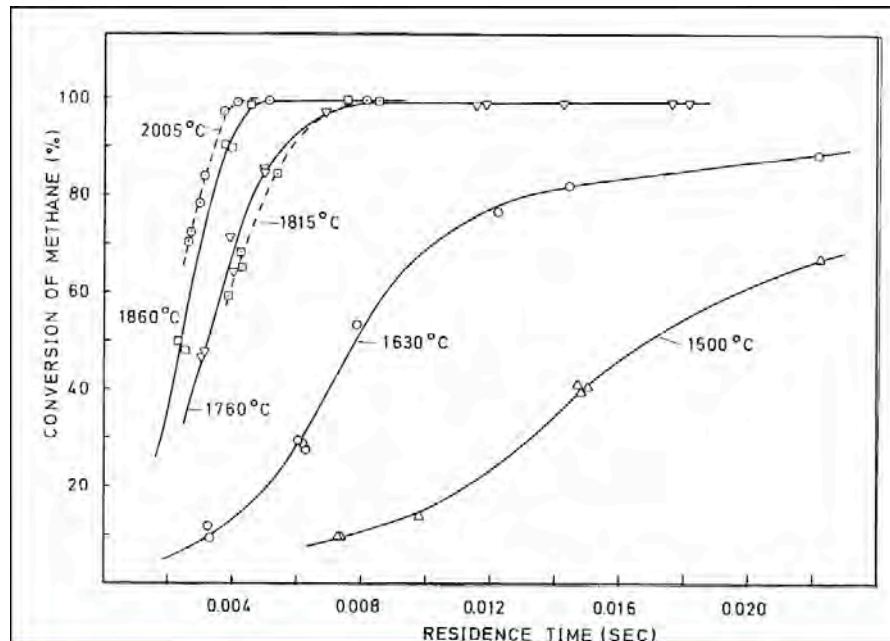
- The device is a simple graphite tube dissociator heated at very high temperature
- Natural gas is introduced at high temperatures and flow rates in the reactor to activate fast, pyrolytic dissociation into Carbon and H<sub>2</sub>
- A dense black carbon black smoke streams from the outlet end of the reactor.
- Carbon black particles are extremely fine and difficult to filter.
- Carbon black is recovered and separated (bag or precipitator).



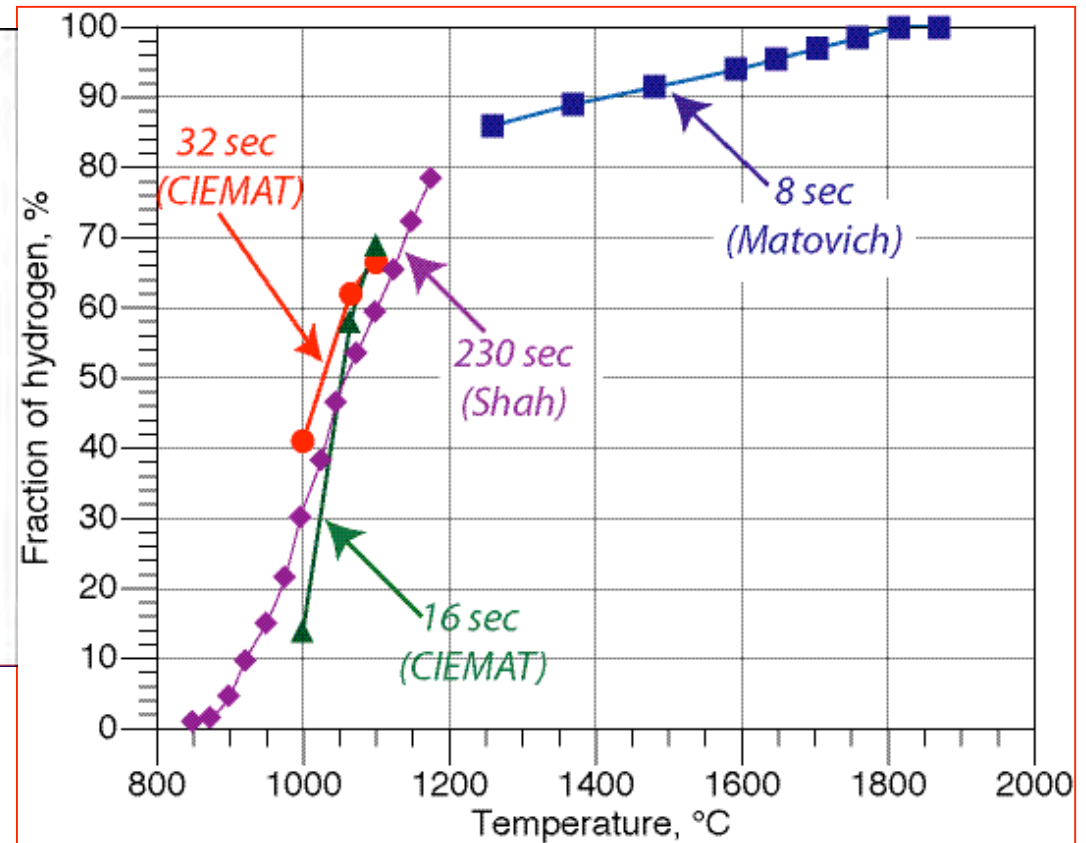
# Universal behavior of different measurements

## CIEMAT + U.P.M TEAM

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J. MARTINEZ-VAL, C. RUBBIA, J.A. RUBIO, E. RUIZ, D. SALMIERI



- Extremely fast conversion time of methane splitting.



Remarkable, over-all agreement

The best alternative to  
complement Oil:

Hydrogen + CO<sub>2</sub> -> Methanol

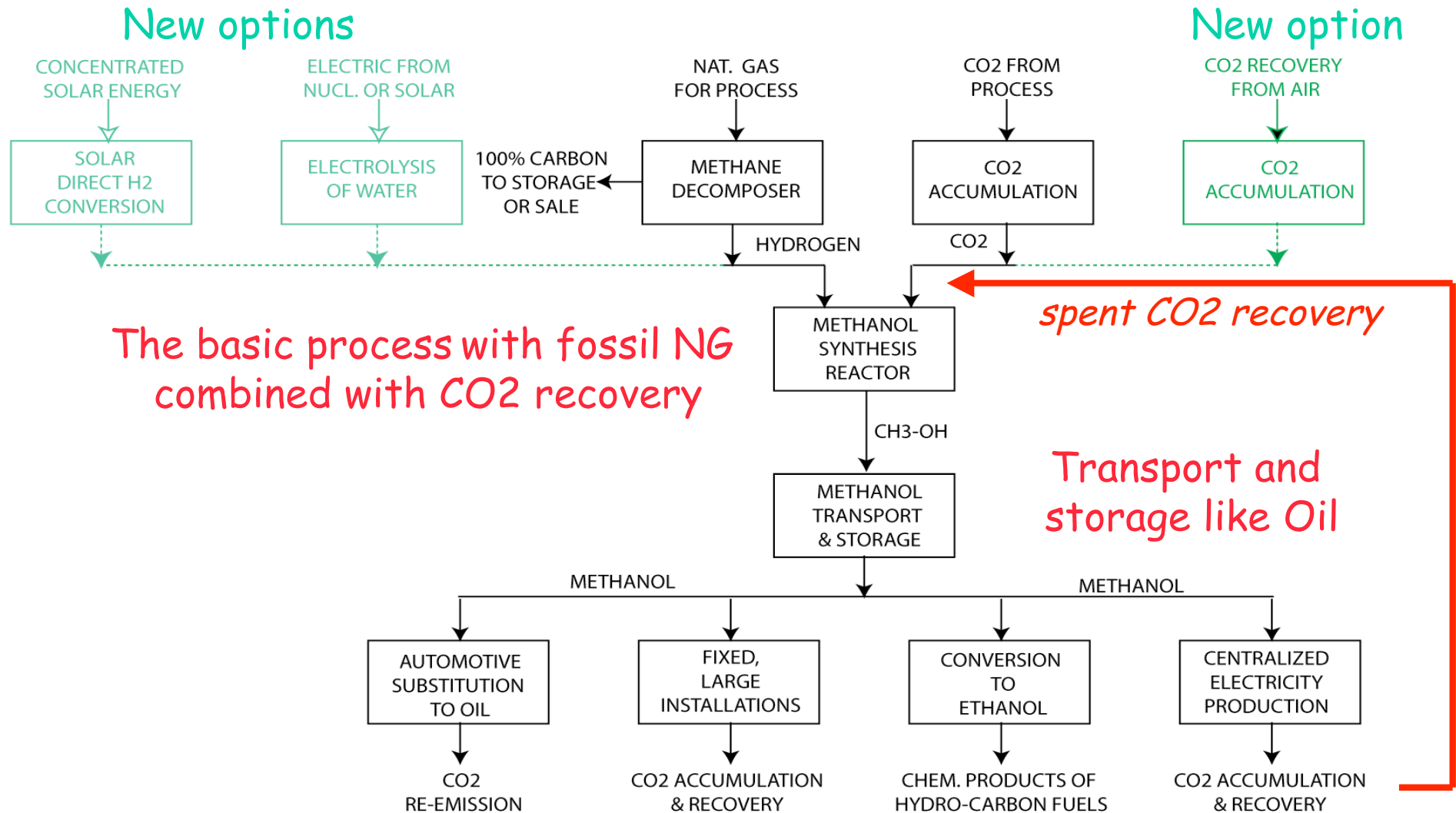
# Methanol (not hydrogen) is the future !

- Organic methanol from bio-mass (eventually ethanol) has been very extensively used as organic substitute to Oil for almost all its applications. See f.i the Brazil's pioneering work.
- Very large amounts of fossil NG are available: their cost at the point of production is usually very low (0.5 \$/GJ); most of its added cost is transport with pipelines or liquefaction.
- A spontaneous, local conversion of fossil NG into H<sub>2</sub> and black carbon without CO<sub>2</sub> emissions is readily performed.
- Assume that we recover CO<sub>2</sub> as a **chemical material** and to **recycle it** from some conventional source of concentrated CO<sub>2</sub> waste, already "paid for" by the savings due to the CO<sub>2</sub> conversion of the previous application (two for one).
- CO<sub>2</sub> and hydrogen can produce methanol and water, a liquid substitute to gasoline in all distant transport applications; if in a concentrated source, it could be indefinitely recycled.





# Alternate processes with CO2 preservation

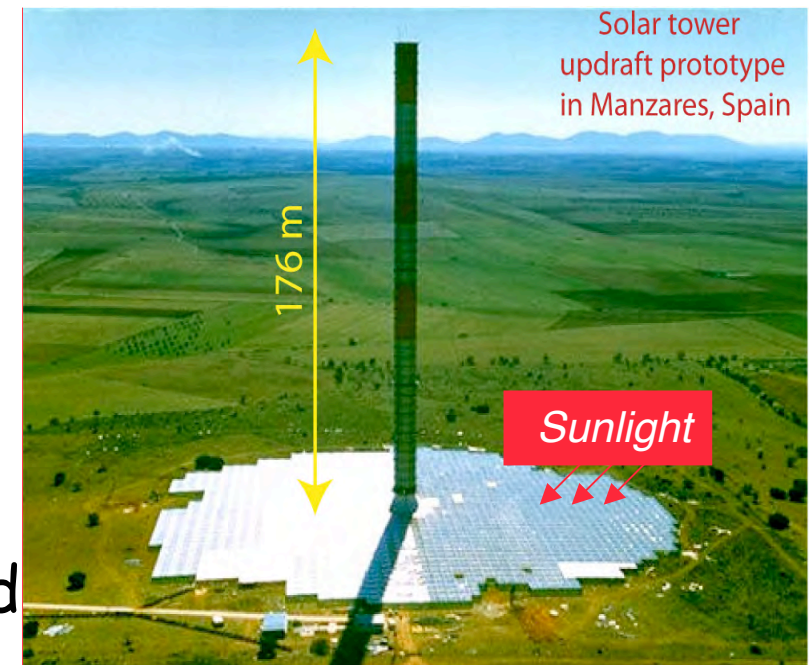


## Conclusion: the future for transportation is methanol !

- Methanol is a bulk commercial chemical which can be obtained in many ways. A promising new method could be some already recovered  $\text{CO}_2$  reacting with hydrogen.
- Compared to  $\text{H}_2$ , methanol is a convenient liquid product.
- Methanol is an excellent fuel in its own right and it can be blended with gasoline or used in the "methanol fuel cell", producing electricity directly combined with air.
- Methanol can be converted to ethylene, the key material to produce hydrocarbon fuels and their products.
- Therefore it would be able to replace oil both as a fuel and chemical raw material without costly new infrastructures.
- It would provide a feasible and safe way to store energy, make available a convenient liquid fuel, and provide mankind with an unlimited source of hydrocarbons mitigating the dangers of global warming.

# New Option: recovering spent CO<sub>2</sub> from the atmosphere ?

- According to this alternative to sequestration, the atmosphere of the planet would act as a temporary storage and transport.
- Air extraction is an appealing concept, because it separates the location of the CO<sub>2</sub> source from its disposal. CO<sub>2</sub> can be recovered from any product (including cars, airplanes, flames, fires, heating, etc), located far away from the sources.
- These dedicated sinks should behave like "synthetic trees", removing the CO<sub>2</sub> of the air ( $\approx 360$  ppmV).
- A solar tower ("solar chimney") is a air collector and a central updraft tube generating a strong convective flow through a chemical sorbent. Cold CO<sub>2</sub> and sorbent combine. CO<sub>2</sub> is recovered at high temperature



(Haaf et al. 1983, Schlaich et al, 1990)

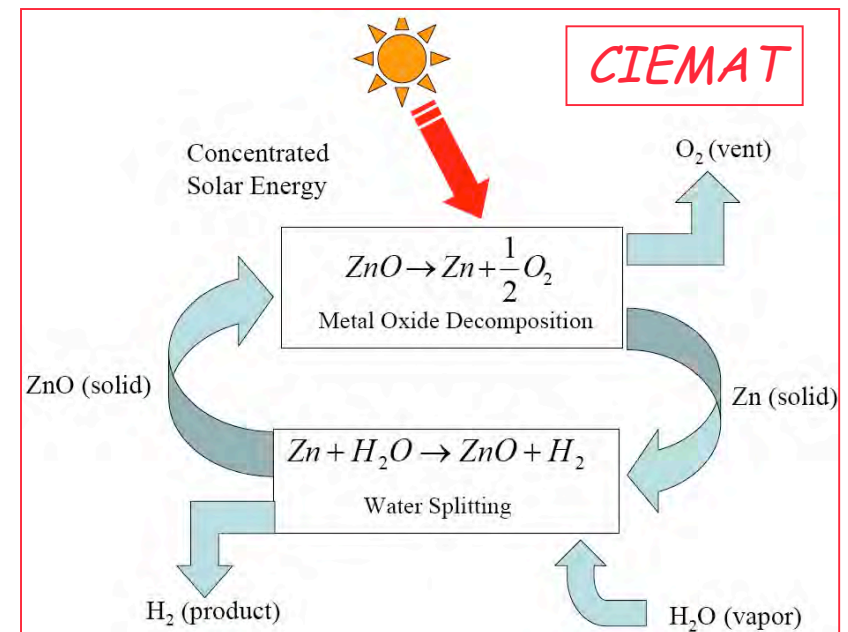
# CO2 from air: a dream or a reality ?

TOWER PARAMETERS		
Height tower	500.	m
Radius tower	55.	m
Diameter collector	4300	m
Area collector	14.5	km <sup>2</sup>
Peak solar power	900. 0	W/m <sup>2</sup>
Tower wind efficiency	1.635	%
AIR:-WIND ENERGY PRODUCTION		
Wind speed	79.73	km/h
Air mass	321.6	ton/s
Air mass /m <sup>2</sup> /sec	26.6	kg/m <sup>2</sup> /s
Kinetic air theor. power	78.9	MW
Wind turbine conversion eff	0.50	
Actual Wind power	39.43	MW
Fract. windy hours	2190	/y
Electric Wind energy yearly	86.36	GWh
CO2: ACCUMULATION		
CO2 volumic	0.36E-03	ppv
CO2 volume/sec	96.47	m <sup>3</sup> /s
CO2 mass/sec	0.193	ton
CO2 mass/h	694.6	ton
Effective CO2 mass/y	1.52	Mton/y
EQUIVALENT COAL BURNING		
Electric coal burning equiv to Wind	0.108	Mton/y
Wind CO2/Coal CO2 (same electric energy)	14.03	



## New Option: Direct Hydrogen production without CO2 (cont)

- Hydrogen can be produced directly from water dissociation with the help of high temperature (solar) heat.
- But a **spontaneous dissociation of water** into  $H_2$  and  $O_2$  is only possible at temperatures above  $3000\text{ }^\circ\text{C}$ , far too high to be of practical use. Several **simple thermo-chemical processes** are under development in which concentrated solar heat, at temperatures of the order  $1200\text{ }^\circ\text{C}$ , splits  $H_2O$  into  $H_2$  and  $O_2$ .
- Some optimal processes are oxi-reductions of  $ZnO/Zn$ ,  $Fe_3O_4/FeO$  and  $Fe_2O_3/Fe_3O_4$ . They are cycles with a high efficiency, large scale and environmentally attractive.
- The accumulated hydrogen energy in good sunny regions is in practice about 50% of the incoming solar.



**Thank you !**