CO_2, life, climate and the dynamics of the Earth Mantle

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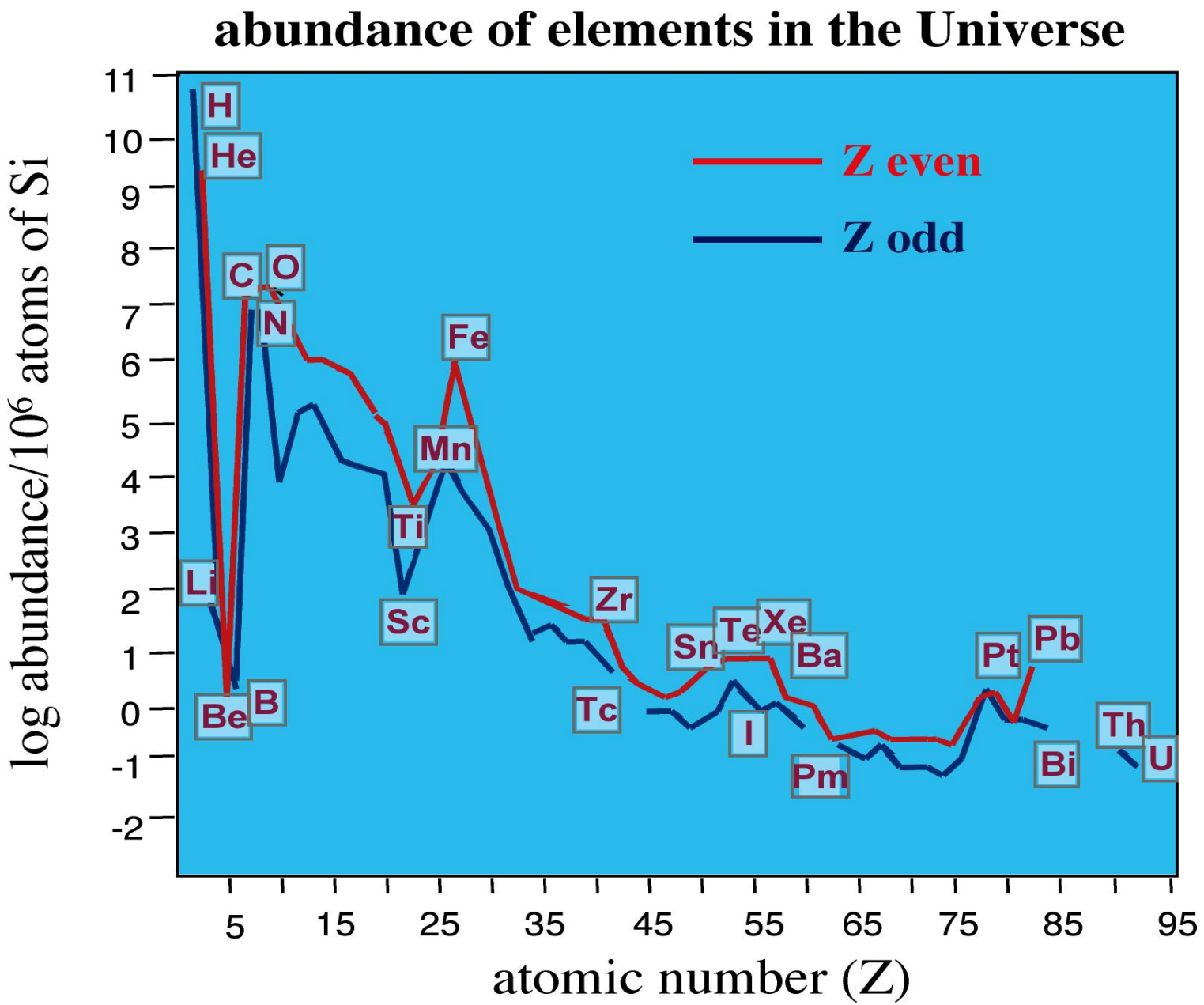

abundance of elements in the Universe
log abundance/10^6 atoms of Si
atomic number (Z)
Z even
Z odd
H
He
C
O
N
Fe
Mn
Ti
Li
Sc
Zr
Sn
Te
Xe
Ba
Pt
Pb
Be
B
Tc
I
Pm
Bi
Th
U
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
5
15
25
35
45
55
65
75
85
95

Carbon in the crust

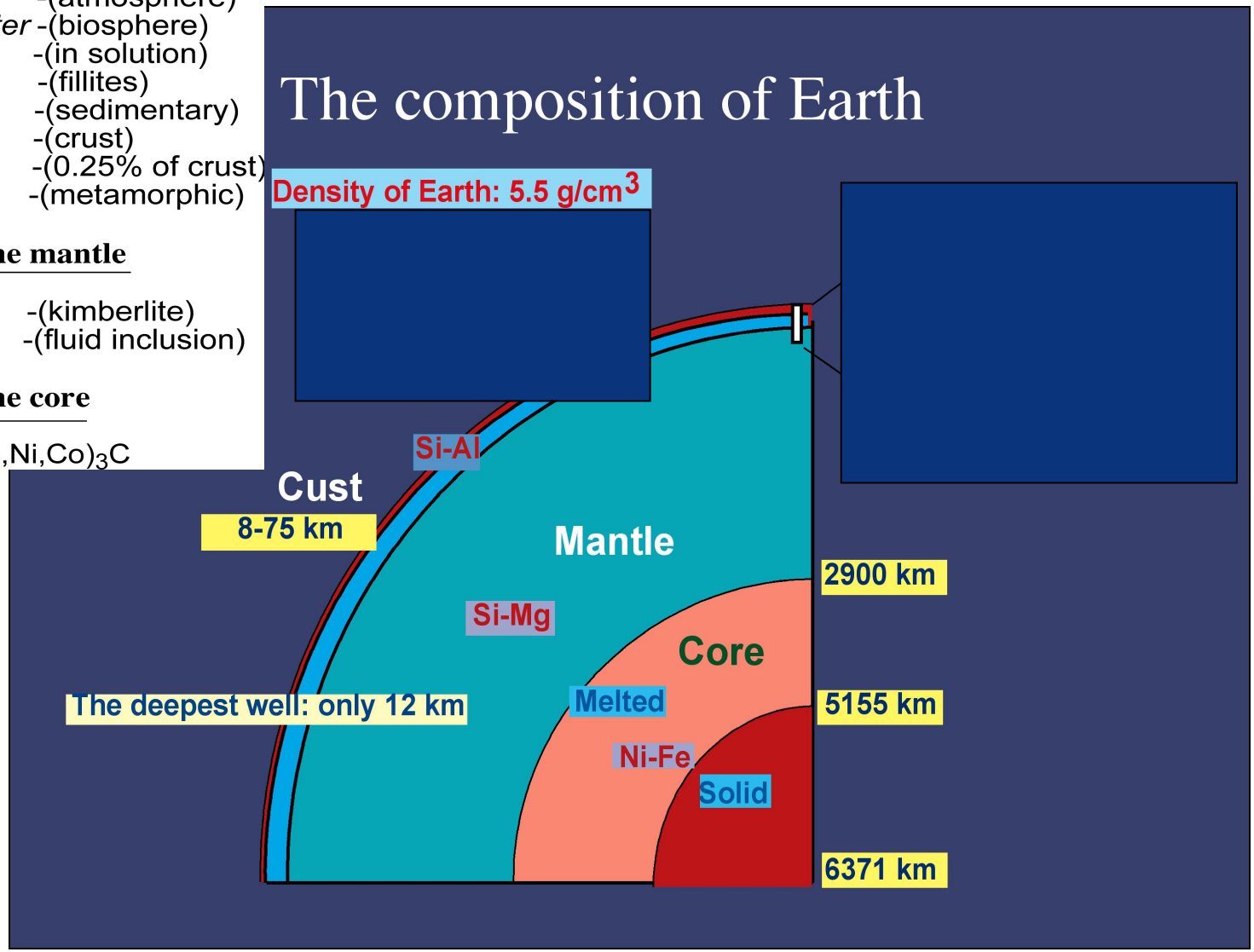
CO_2	-(atmosphere)
organic matter	-(biosphere)
HCO_3	-(in solution)
kerogen	-(fillites)
coal	-(sedimentary)
oil+gas	-(crust)
limestone	-(0.25% of crust)
graphite	-(metamorphic)

Carbon in the mantle

diamond	-(kimberlite)
CO_2	-(fluid inclusion)

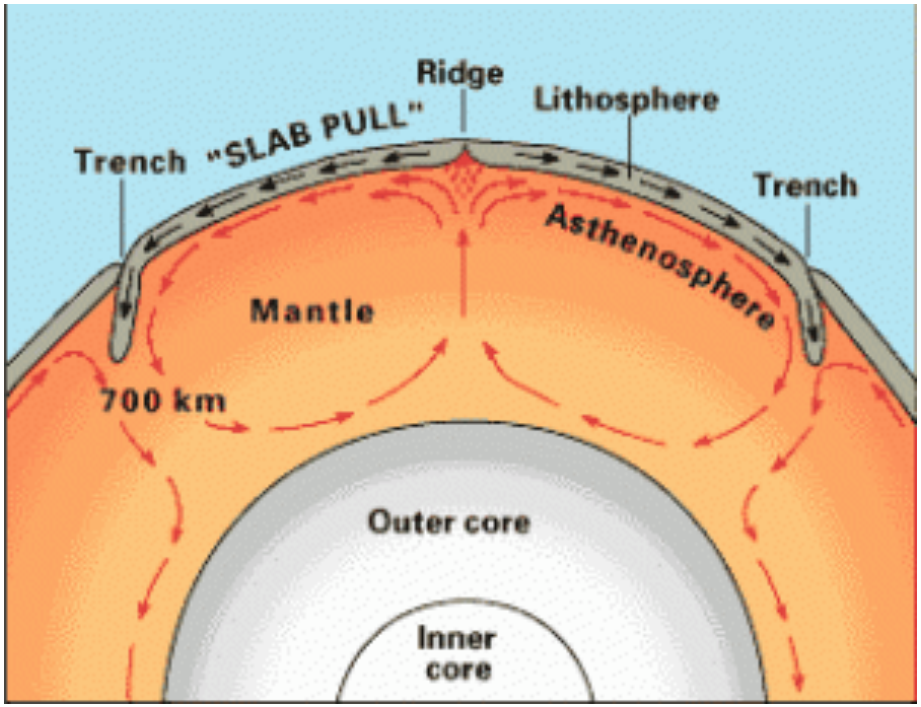
Carbon in the core

Cohenite $(Fe,Ni,Co)_3C$

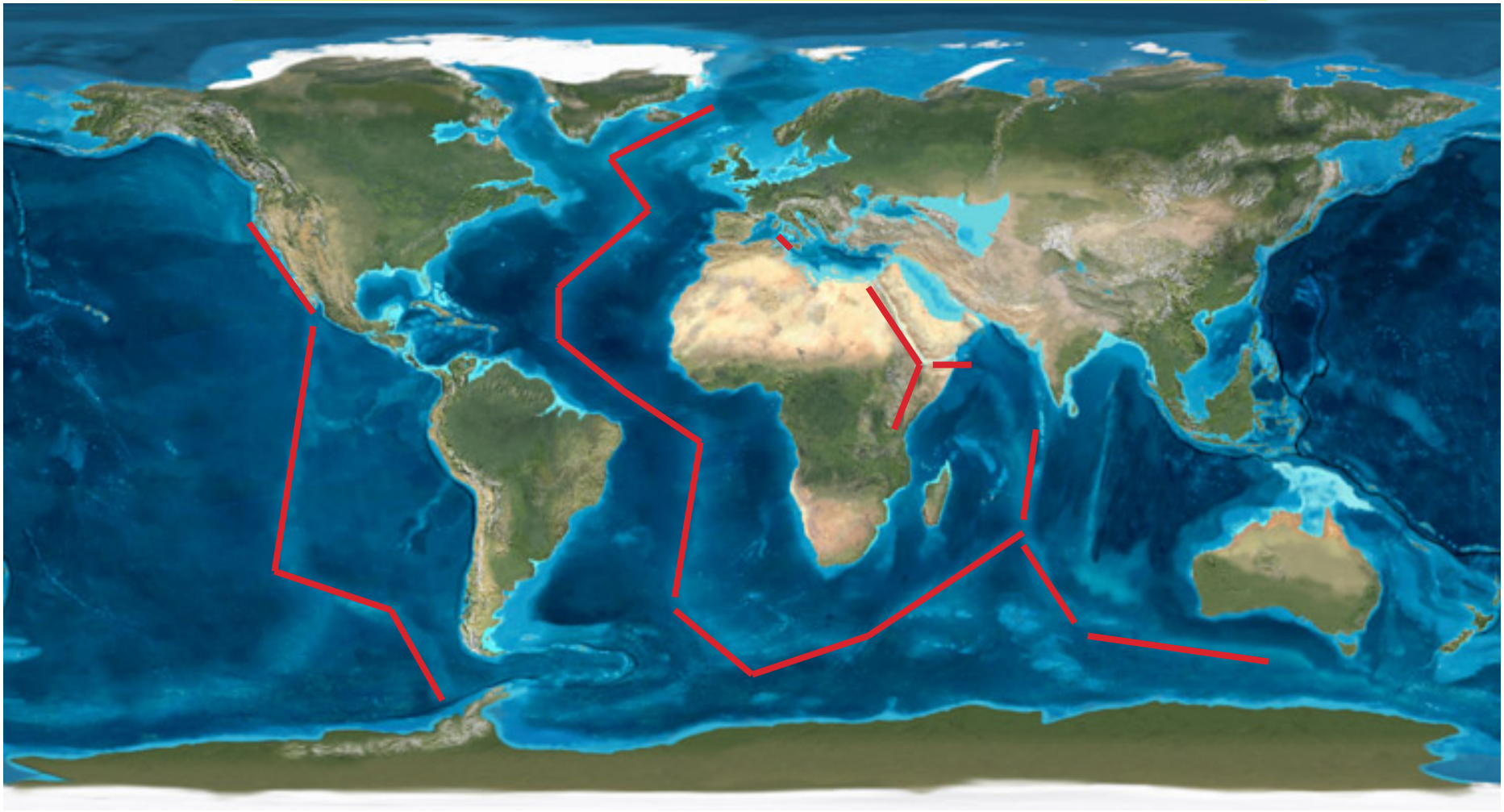


Because the temperature of the "core" is > 6000 °C there is a cooling gradinet in the mantle that causes convection (besides conduction)
THERMAL COOLING

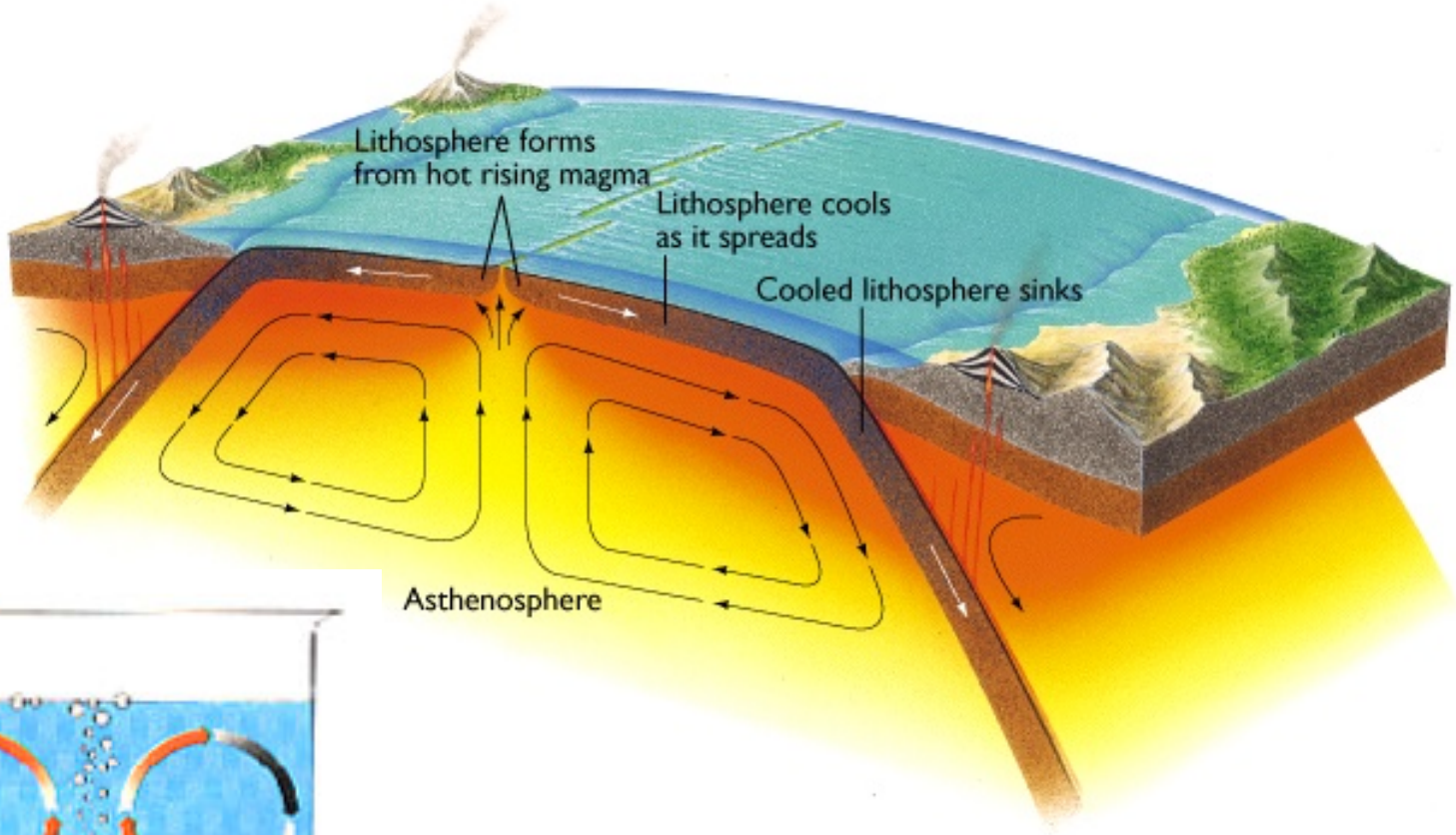
Thermal convection in the mantle



The mantle trasfers "iuvenile" heat and material to the surface prevalently along the ocean ridges



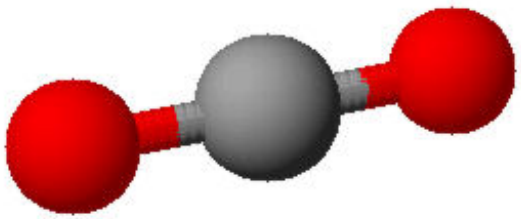
*Most of chemical elements **are recycled by the Mantle***
(apart from atmophile elements: noble gases, N, C, Hg..etc.)



The carbon cycle practically coincides with the cycle of (CO_2)

…and CO_2 has a paramount role for the persistence of life and on climate change

<O=C=O>



Role of CO_2 in Earth history

1st phase *- (5000 °C - 100°C) CO_2 mostly in the atmosphere, together with HCl, SO_2, CH_4, N_2…..etc.*

2nd phase *- (T<100 °C) condensation of H_2O, solubilization, formation of carbonic acid (H_2CO_3), alteration of silicates, formation of HCO_3 ion*

3rd phase *- ($CaCO_3$ precipitation in the ocean: beginning of CO_2 sequestration from the atmosphere)*

1st SEQUESTRATION PROCESS: Surface alteration of silicates

$$CO_2 + H_2O = H_2CO_3$$

$$CaSiO_3 + 2(H_2CO_3)_{(aq)} = Ca^{++} + 2HCO_3^- + SiO_{2(aq)} + H_2O$$

Paleo-rivers started the transfer of Ca e HCO_3 ions into the paleo-oceans

$$Ca^{++} + 2HCO_3^- = CaCO_3 + H_2CO_3$$

$$H_2CO_3 = CO_2 + H_2O$$

CO_2 sequestration from the atmosphere

The formation of limestone platforms (Dolomites,Bahamas, coral rifts…etc) in geological time (10^9 anni) brought the crust (the last 5-60 Km of Earth) to be made of about 0.25 % by limestone and/or dolostone

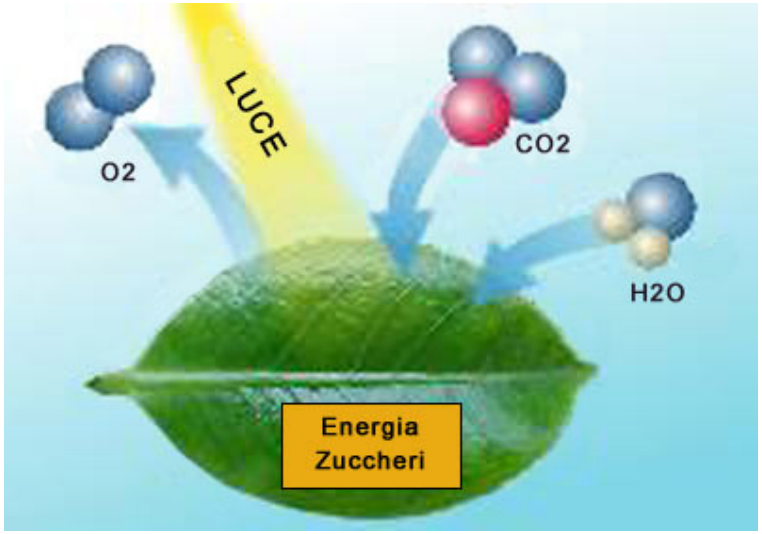
Bagni San Filippo (Amiata volcano, central Italy)

Suddendly,
by chance, or by
Divine Providence,
Life starts

$$Ca^{++}+2HCO_3^{-}=CaCO_3+H_2CO_3$$

$$H_2CO_3=CO_2+H_2O$$

Life is related with:
the 2nd SEQUESTRATION PROCESS
OF CO_2 FROM THE ATMOSPHERE



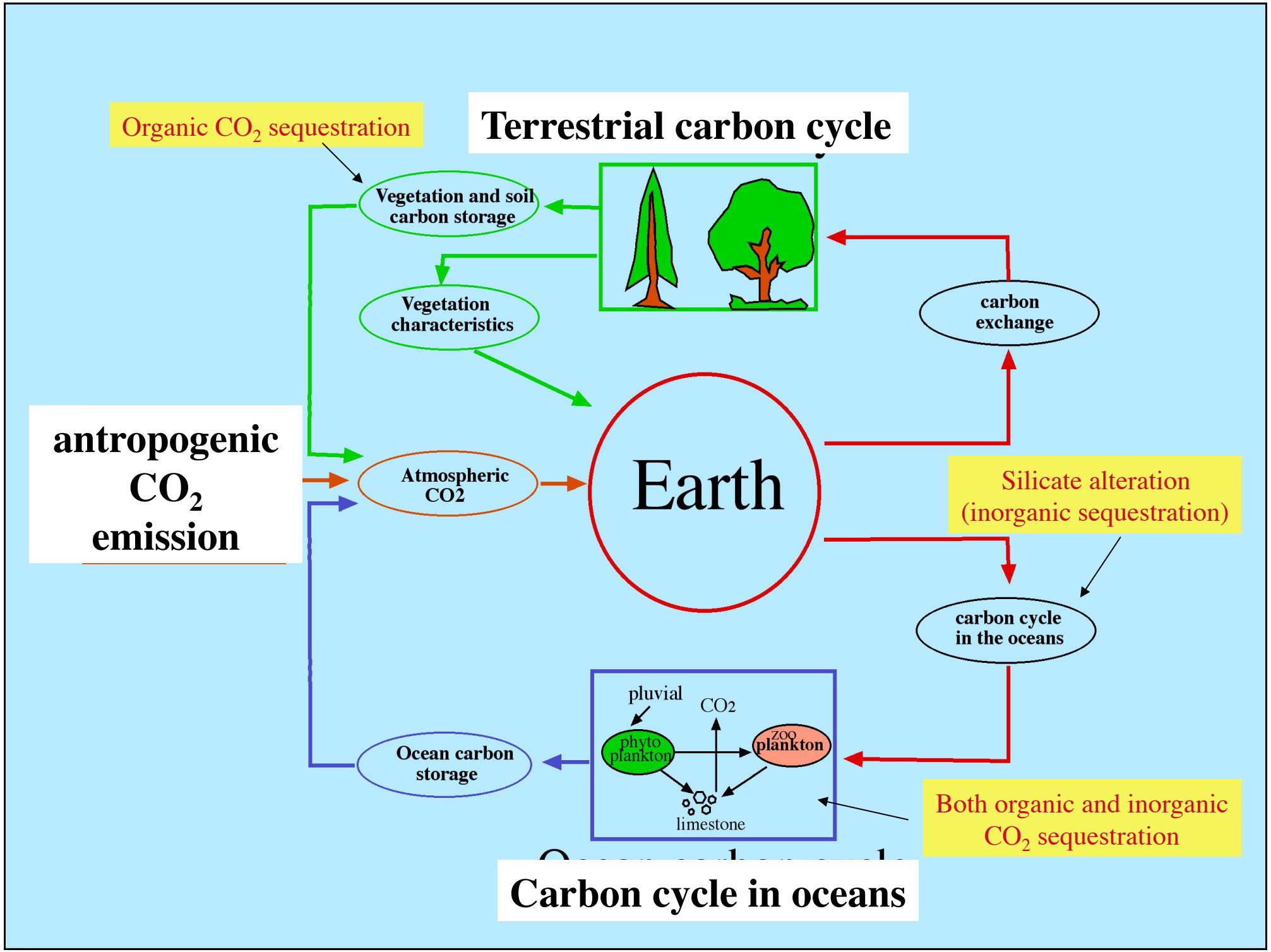
$$CO_2 + H_2O + \text{radiation} = C\text{-}H\text{-}O + O_2$$

$$C + O_2 = CO_2 \text{ (in oxidative environment)}$$
(aired)

In reducing environment:
(anaerobic, euxinic, anossic)

from vegetal accumulation: **coal**

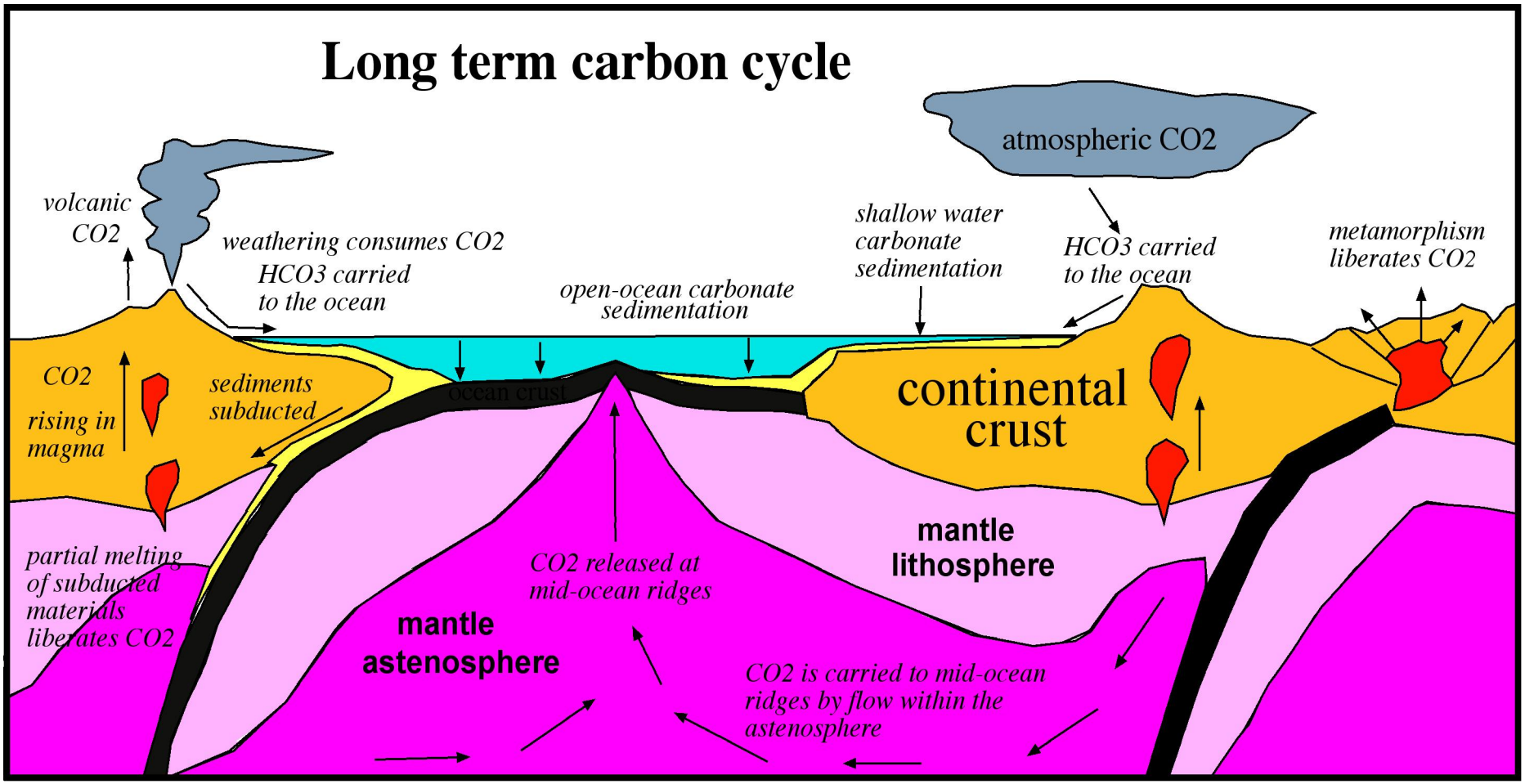
from animal accumulation: **oil**


Organic CO_2 sequestration
Terrestrial carbon cycle
Vegetation and soil carbon storage
Vegetation characteristics
carbon exchange
antropogenic CO_2 emission
Atmospheric CO2
Earth
Silicate alteration (inorganic sequestration)
carbon cycle in the oceans
pluvial
CO_2
phyto plankton
zoo plankton
limestone
Ocean carbon storage
Both organic and inorganic CO_2 sequestration
Carbon cycle in oceans

Without imputs of new CO_2 into
the atmoshere, because of natural sequestrtion
processes, life on Earth
Would disappear in about 300,000 years

**(and without CO_2 in the atmosphere
average temperature at the surface
would drop down to -27 °C)**

The dynamics of the mantle helps life



1,000,000*gr* / 48*gr* = 20.833 *moles*
20,833 *moles* x 22,4 *L* = 466,000 *L*
1 *Ton of CO_2 is about 466 m^3*
A cube of 8 m side

Non volcanic CO_2 emission in central Italy

GEOTHERMAL FIELDS:

Larderello	(Tuscany)	3000 T/day

THERMAL SPRING AREAS:

Rapolano	(Tuscany)	150 T/day

MOPHETTES (cold):

Pienza	(Tuscany)	11 (11) T/day
Selvena	(Tuscany)	17 (8)
Caldara	(Latium)	175 (15)
Manziana	(Latium)	30
Casa Ferento	(Latium)	200
Pomezia	(Latium)	50
Mefite	(Campania)	400 (120)

(*in brackets focused emission*)

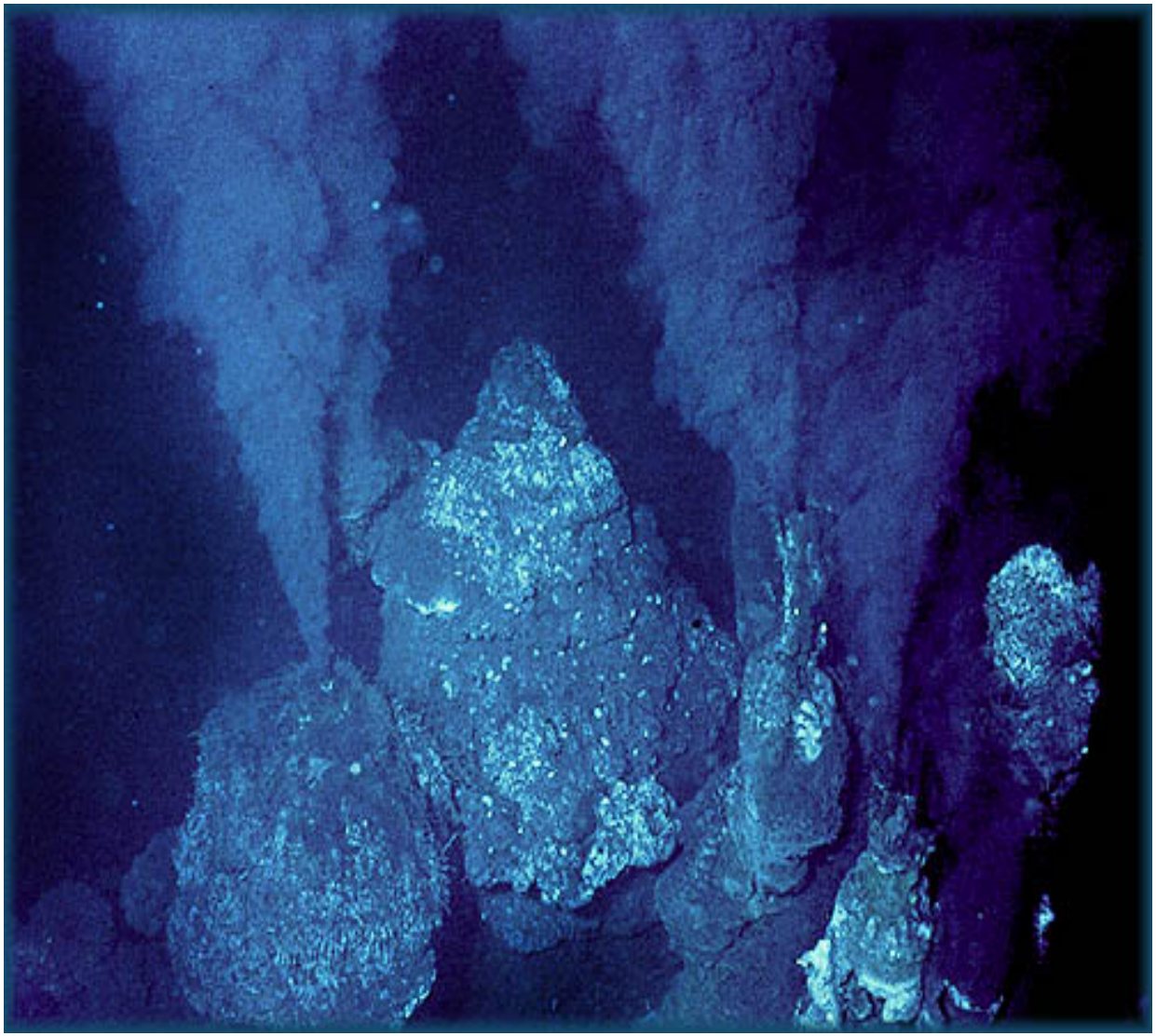
Etna volcano
(Sicily, Italy)

Lava lake (Erta Ale, Ethiopia)

Thermal spring with bubbling gas (Yellowstone Park, U.S.)

Mud volcano
(Azerbaijan)

Black Smokers
(middle ocean ridges)



Mud pool
(Yellowstone)

CO_2 gas vent at

Panarea Island

(Aeolian volcanic

Archipelago, Italy)

Processes sequestrating CO_2 from the atmosphere:

1) Choal and oil in reducing (Eh<0) environments
2) Alteration of silicates by H_2CO_3 (bacteria)
3) Precipitation of $CaCO_3$ in oceans (corals, limestone, plancton..etc.)

Processes reintroducing CO_2 into the atmosphere

1) Oxydation of organic matter
2) Volcanic eruptions
3) Non-volcanic CO_2 (geotermal, metamorphic, ocean ridges)

Equilibrium of carbonates: shallow perspective

Limestone dissolution at neutral pH

$$CaCO_3 = Ca^{++} + CO_3^{--} \quad (K_{sp}=10^{-8.3})$$

Basic hydrolisis of CO_3^{--}

$$CO_3^{2-} + H_2O = HCO_3^- + OH^- \quad (K_{H1})$$

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \quad (K_{H2})$$

If solutions are free to air

$$H_2CO_3 = CO_{2(g)} + H_2O \quad (K=32.2)$$

$$H_2CO_3 = CO_{2(aq)} + H_2O$$

$$CO_{2(aq)} = CO_{2(g)}$$ (as a function of P and T)

Calcite-carbonic acid reaction

$$CaCO_3 + H_2CO_3 = Ca^{++} + 2HCO_3^-$$ (from *p*H= 6.3 to *p*H=10.3)

Oxydation of organic acids in soil by bacteria

$$2C_2O_4^{--} + O_2 + 2H_2O = 4HCO_3^-$$

(oxalic acid = $H_2C_2O_4$)

Equilibrium of carbonates: deep perspective

Formation of CO_2

$CaCO_3 = CaO + CO_{2(g)}$ (T>800 °C)

$CaCO_3 + SiO_{2(aq)} = CaSiO_3 + CO_{2(g)}$ (T>150°C)

Limestone dissolution at acidic pH

$CaCO_3 + H^+ = Ca^{++} + HCO_3^-$ (T> =0°)

$CO_{2(aq)} = CO_{2(g)}$ (in funzione di P)

Acidic hydrolisis of CO_2

$CO_2 + H_2O = H_2CO_3$

$H_2CO_3 + H_2O = H_3O^+ + HCO_3^-$

$HCO_3^- + H_2O = H_3O^+ + CO_3^{--}$

$Ca^{++} + CO_3^{--} = CaCO_3$

Since carbonic acid is a weak acid and calcite is poorly soluble: their equilibria (at surface) are the main buffer of pH on Earth

$CO_3^{--} + H_2O = HCO_3^- + OH^-$

$HCO_3^- + H_2O = H_2CO_3 + OH^-$

Shallow perspective

$$CaCO_3 = Ca^{++} + CO_3^{--}$$

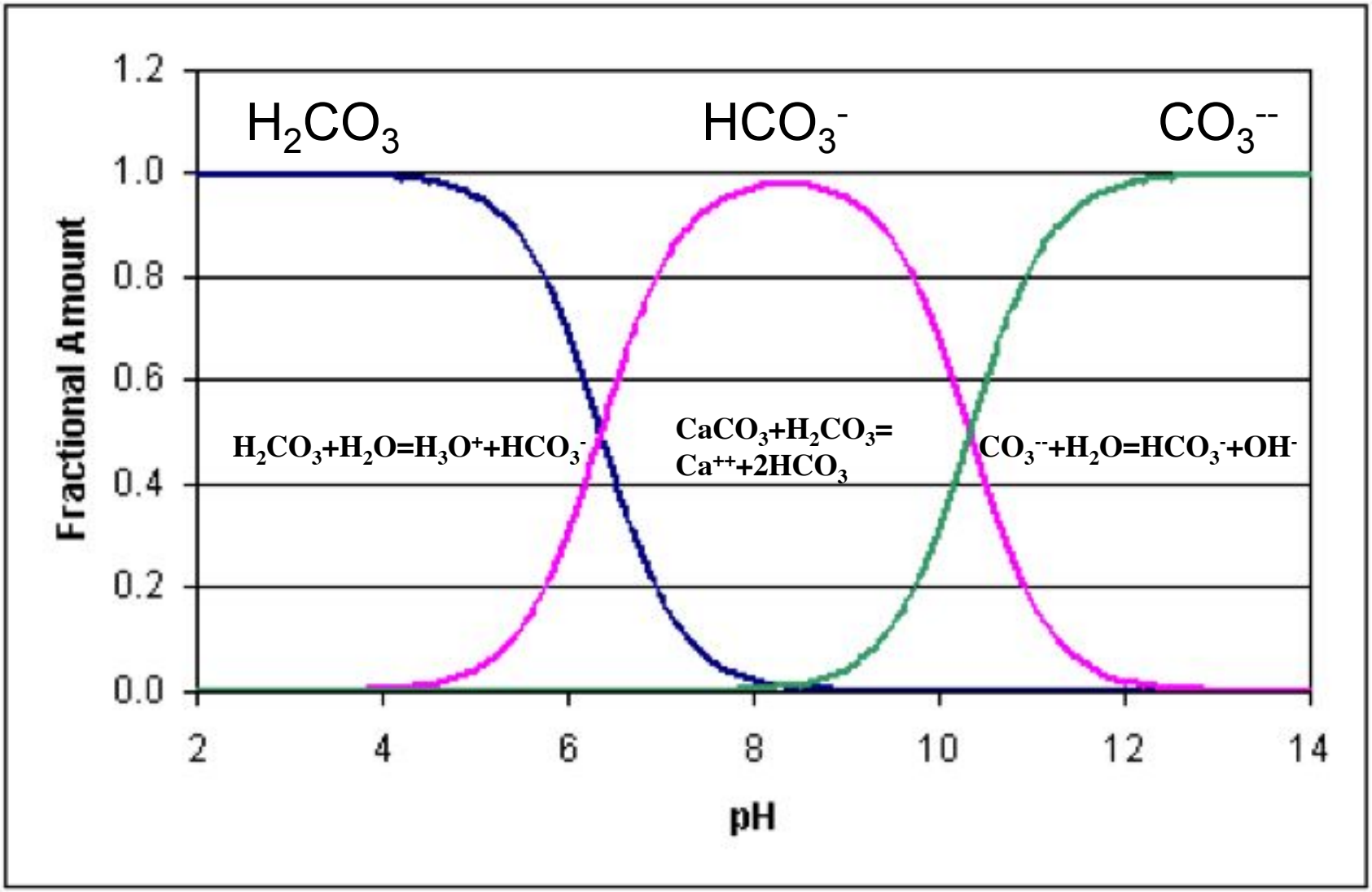
$H_2CO_3 + H_2O = H_3O^+ + HCO_3^-$

$HCO_3^- + H_2O = H_3O^+ + CO_3^{--}$

Deep perspective

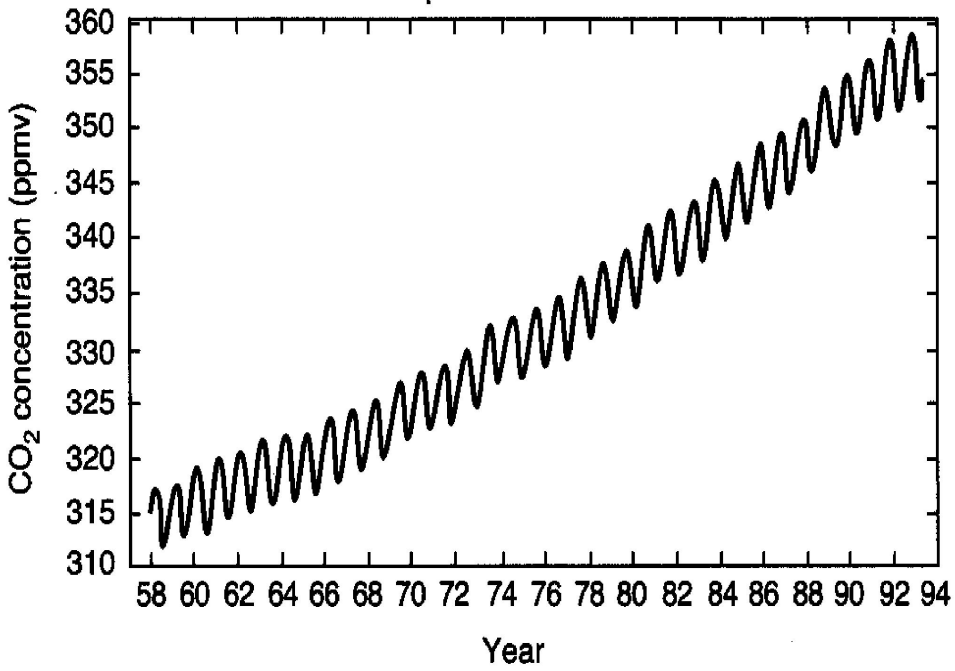
(Similar behavior for B, N, P)

Prevailing species as a function of pH



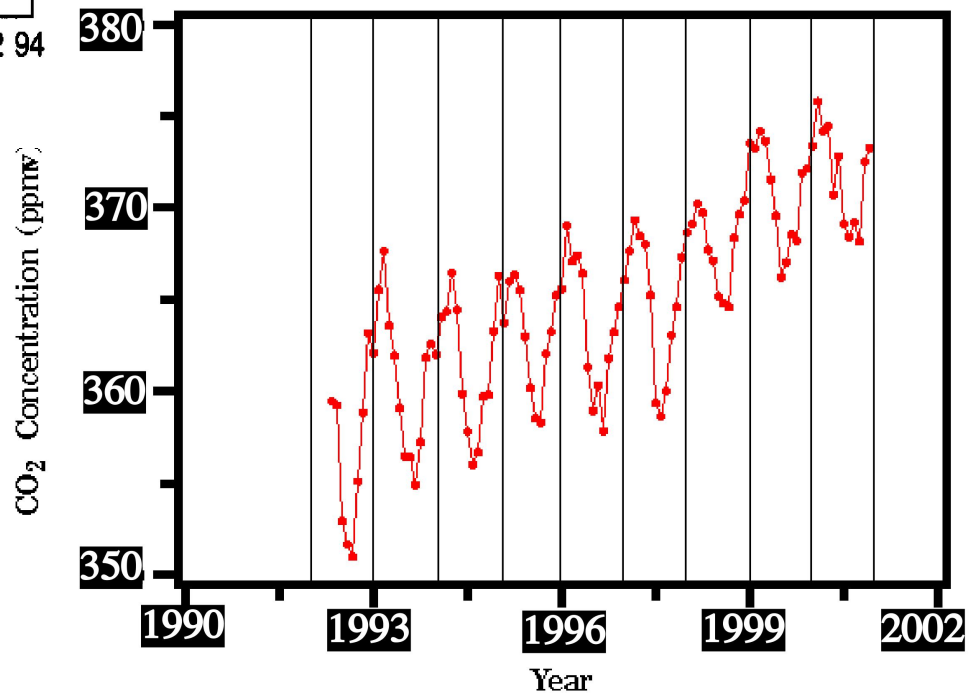
CO_2-green house effect-climatic variations

Hawaii meteorological observatory



(350 ppm =350 mg/kg = 0.035%)

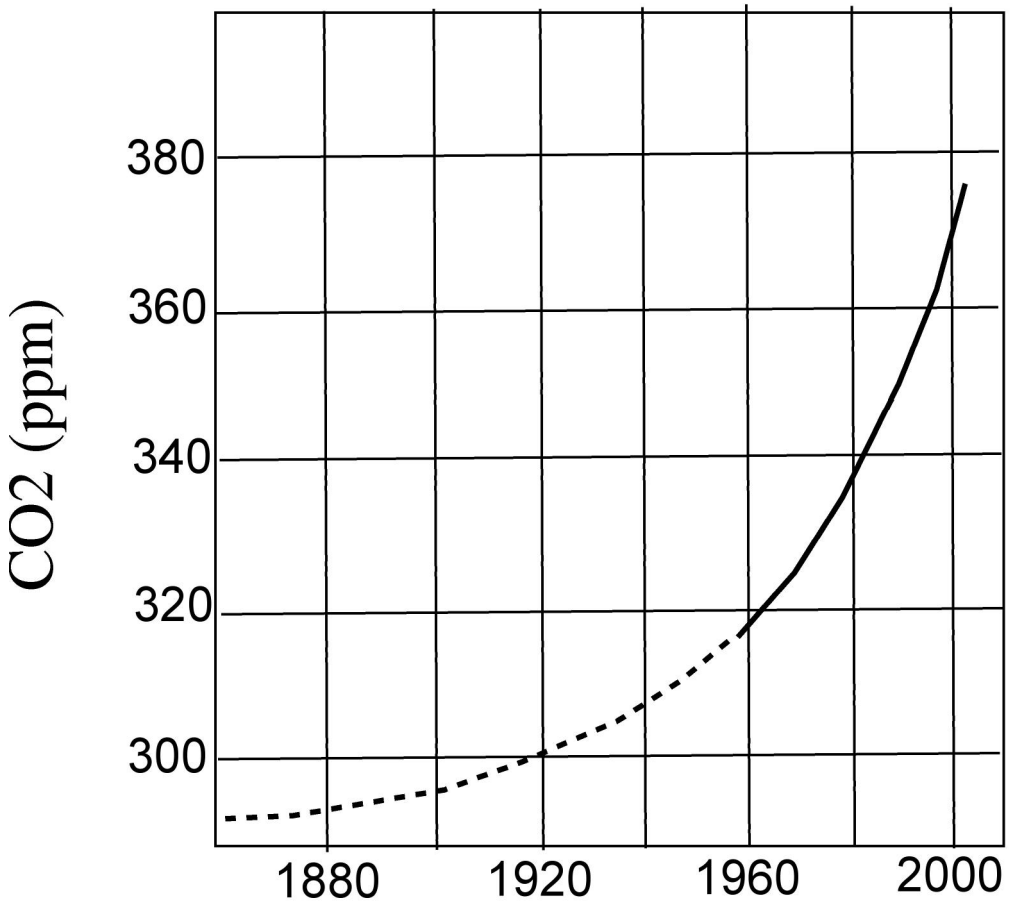
Lampedusa observatory



Source: Paolo Chamard, Luigi Ciattaglia, Alcide di Sarra, and Francesco Monteleone (ENEA, GEM—CLIM)

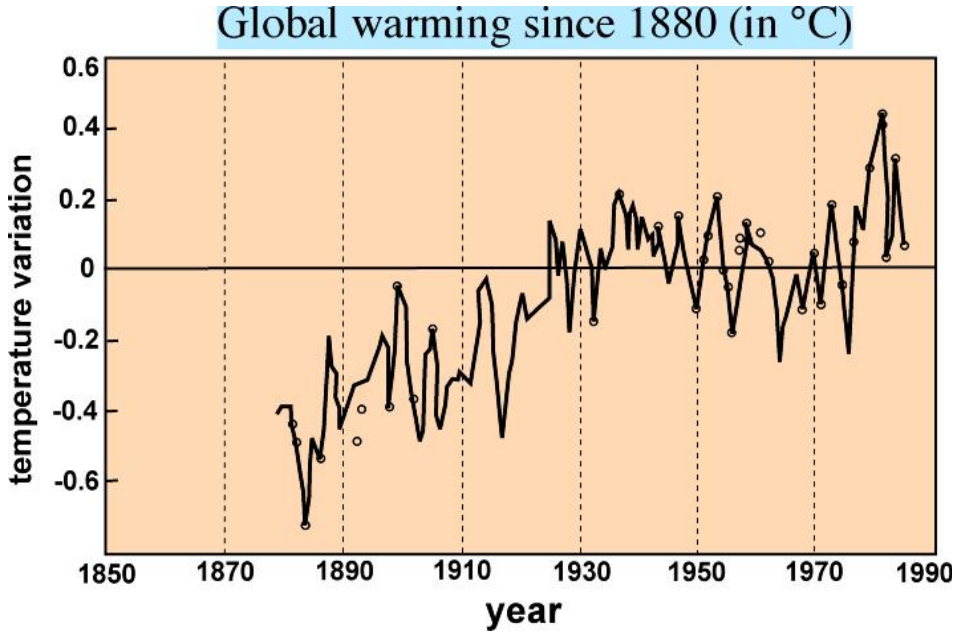
air

$N_2 = 78\%$
$O_2 = 21\%$
$Ar = 0.9\%$
$CO_2 = 0.037\%$



Increase in time of CO2 concentration in the atmosphere

(industriale revolution in England ?)



Atmosphere warming

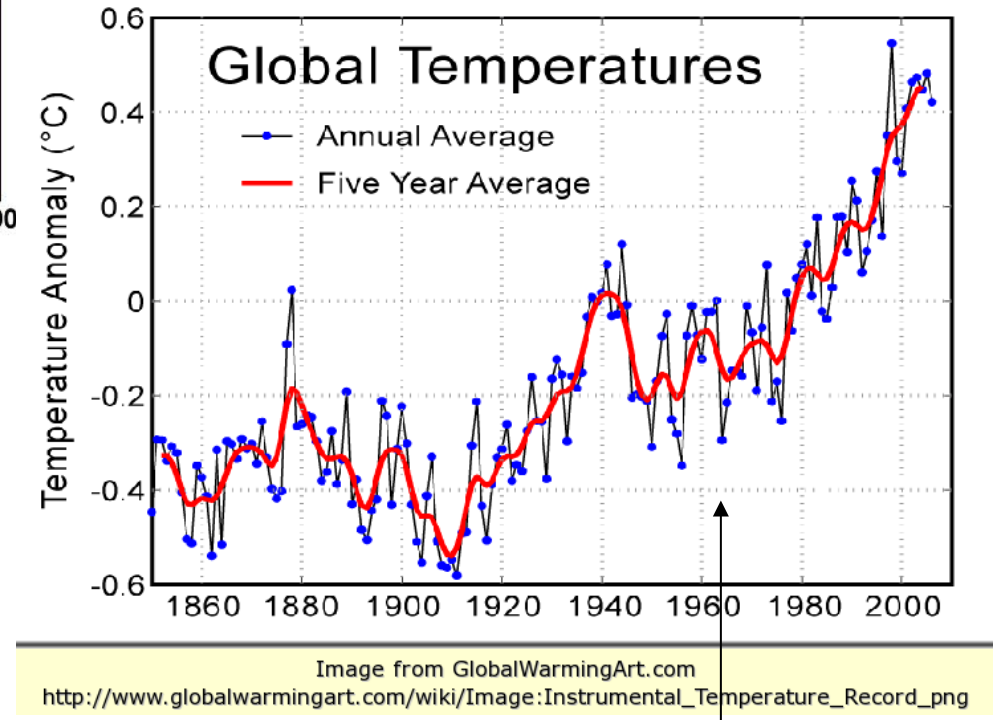
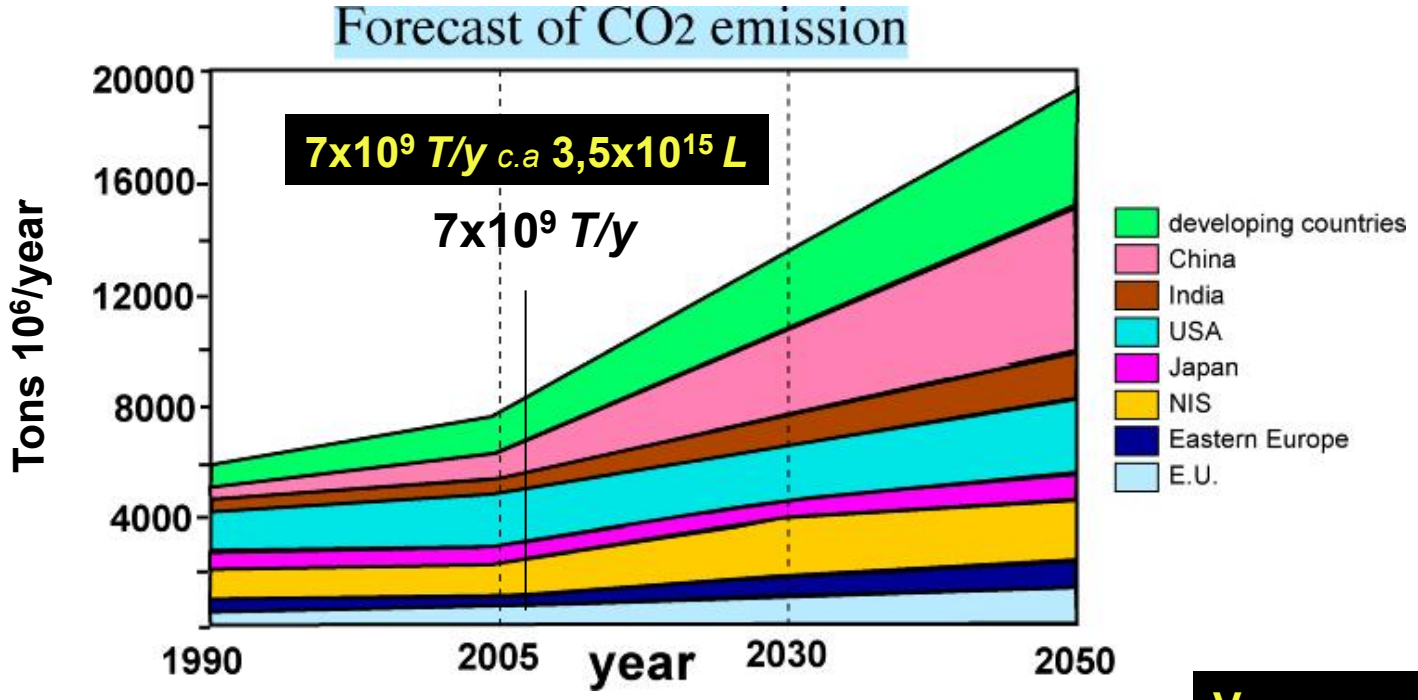
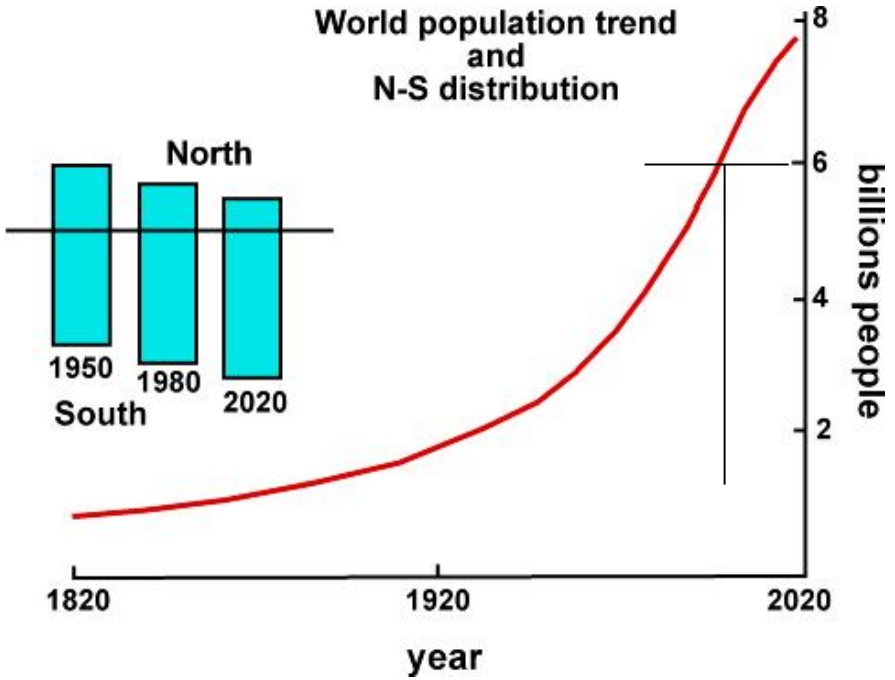


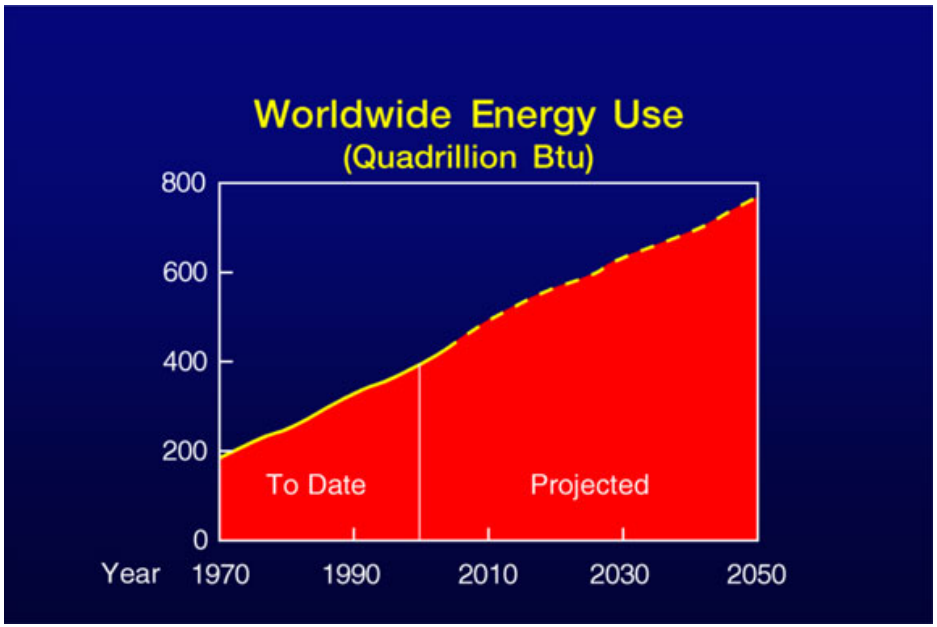
Image from GlobalWarmingArt.com
http://www.globalwarmingart.com/wiki/Image:Instrumental_Temperature_Record_png

Small glaciation of the 70s



$V_{atmosfera}$ *c.a* 10^{18} *L*





CO_2 and climatic changes
(*without men*)

1) If CO_2 changes green hose changes as well
(without CO_2 $T_{atmosphere}$ = -20/-30°C)
2) Low green house when volcanism is low
3) High green house after strong volcanic periods

Coincidence of Deccan basalts extrusion in India when it crossed over the Reunion Island Mantle Hot Spot and contemporary metamorphism of subducted Tethis limestone in Himalaia,
both events occurred in Cretaceous, caused the high CO_2 concentration in the atmosphere (1% ?), whoose green house effect caused dinosaurs extintion (65 Ma)

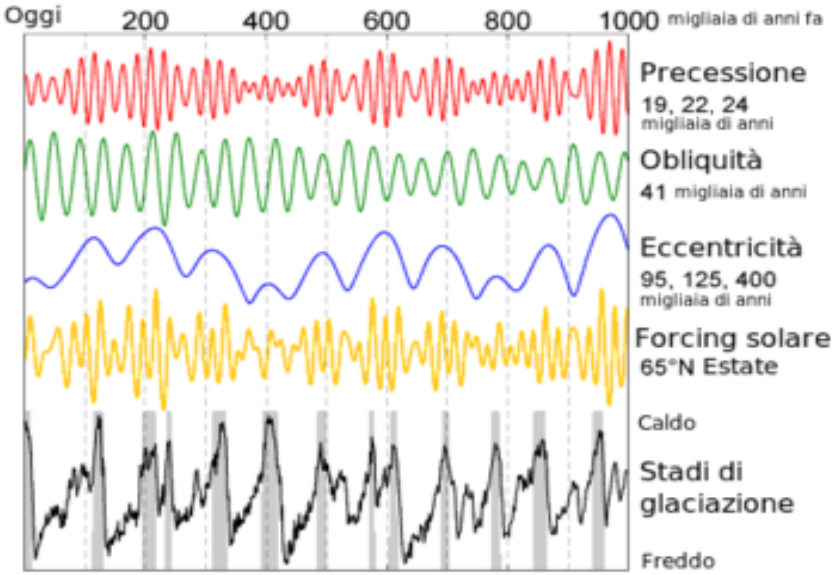
Actually climate (in terms of absorbed radiation) Changes for "astronomic" reasons

Milankovitch (Serbian Matematician) Cycles

1) Variation or orbital eccentricity - consequent to the variation of the gravitational field (100.000 years)
2) Variation of axis obliquity (about 23°) as a function of the orbit (40.000 years)
4) Equinox precession (sliding of the axis, every 20.000 years)

The cycles are "perturbed" by:

1) Stong volcanic eruptions (es. Deccan Trap)
2) Activity of Sun (es. black spots, magnetic storm..
3) Meteorites



Causes of climate variations:

-LONG TERM variations *(alteration of silicates, coral rifts…etc), less CO_2 > to cool periods*

-CYCLIC variations (astronomic reasons), CO_2 varies accordingly - towards either hot or cool periods

-SUDDEN variations *(vulcanic eruptions, meteorites, Solar spots....etc), more CO_2 towards hot periods*

In general:

At the geological time scale, climatic changes, and LIFE changes are modulated by The DINAMICS OF THE EARTH MANTLE

Conclusions

1) On the Earth there are processes that sequestrate CO_2 from the atmosphere.
2) Withouth the Dinamics of the Mantle, that recycles CO_2 at continental margins, Life would disappear in 300,000 years and surface temperaturewould drop at -27°C.
3) Low concentrations of CO_2 in the atmosphere are undesirable.
4) If climate changes for astronomic reasons CO_2, solubility in oceans and/or CO_2 in the atmosphere changes acordingly

therefore

CO_2 variations in the atmosphere are, at the same time:

1) Cause of climaticic variations (e.g.. after big eruptions)
2) Conseguence of climatic variations for astronomic reasons

THIS IS THE REASON WHY IN THE SCIENTIFIC COMMUNITY THERE IS NO A GENERAL AGREEMENT ON THE ROLE PLAYED BY THE ANTROPIC CO_2