CHAPTER 6: BIOGEOCHEMICAL CYCLES

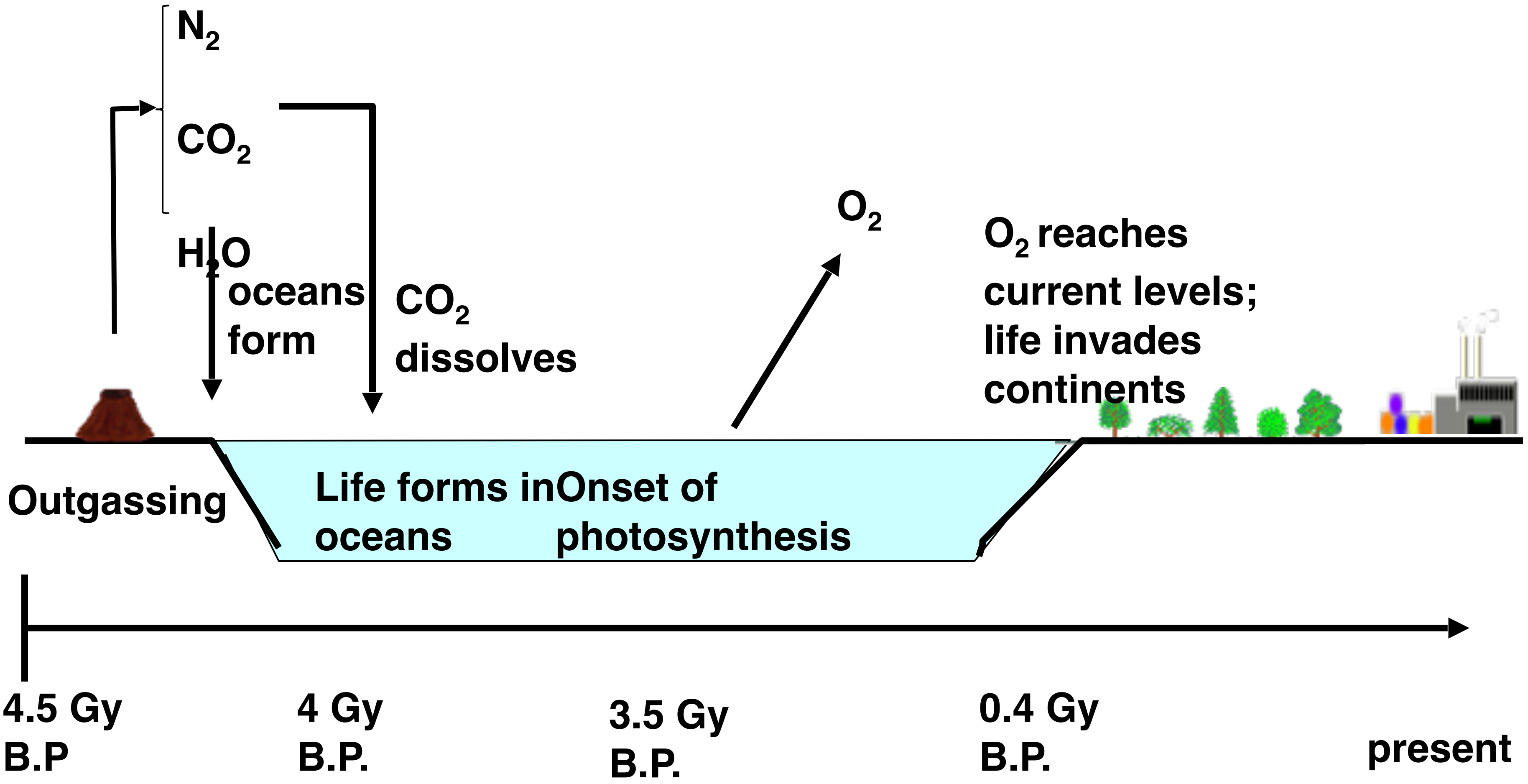
THE EARTH: ASSEMBLAGE OF ATOMS OF THE 92 NATURAL ELEMENTS

- Most abundant elements: oxygen (in solid earth!), iron (core), silicon (mantle), hydrogen (oceans), nitrogen, carbon, sulfur…

- The elemental composition of the Earth has remained essentially unchanged over its 4.5 Gyr history
  - Extraterrestrial inputs (e.g., from meteorites, cometary material) have been relatively unimportant
  - Escape to space has been restricted by gravity

- *Biogeochemical cycling* of these elements between the different reservoirs of the Earth system determines the composition of the Earth’s atmosphere and oceans, and the evolution of life

HISTORY OF EARTH’S ATMOSPHERE



N_2

CO_2

H_2O

oceans form

CO_2 dissolves

O_2

O_2 reaches current levels; life invades continents

Outgassing

Life forms in oceans

Onset of photosynthesis

4.5 Gy B.P

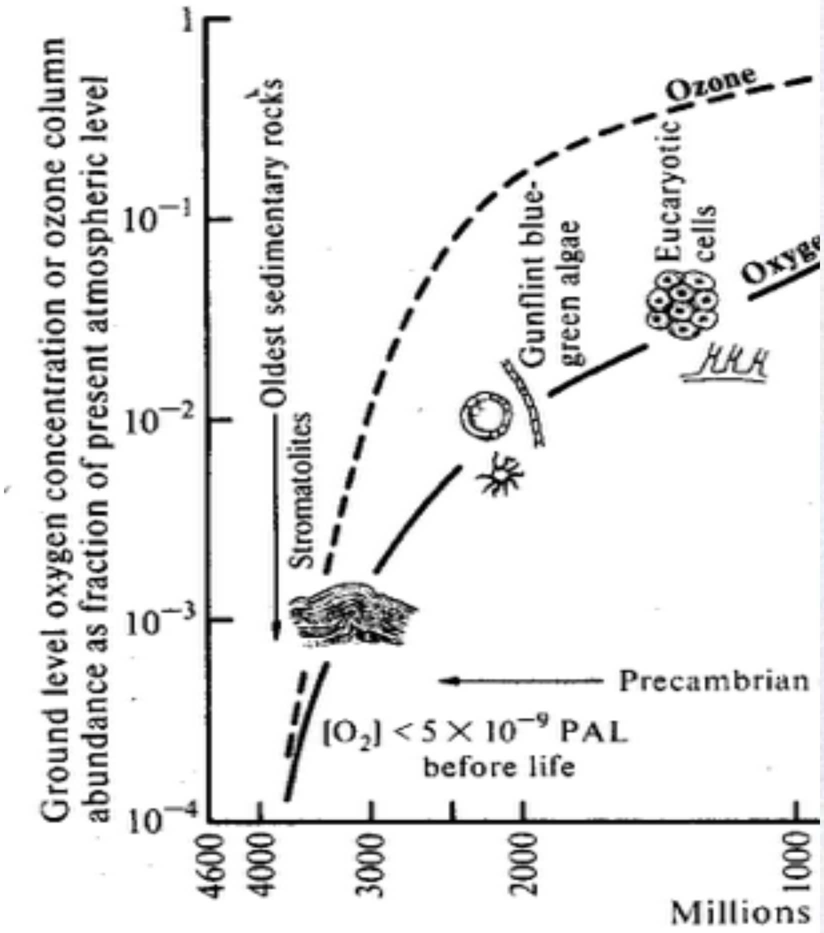
4 Gy B.P.

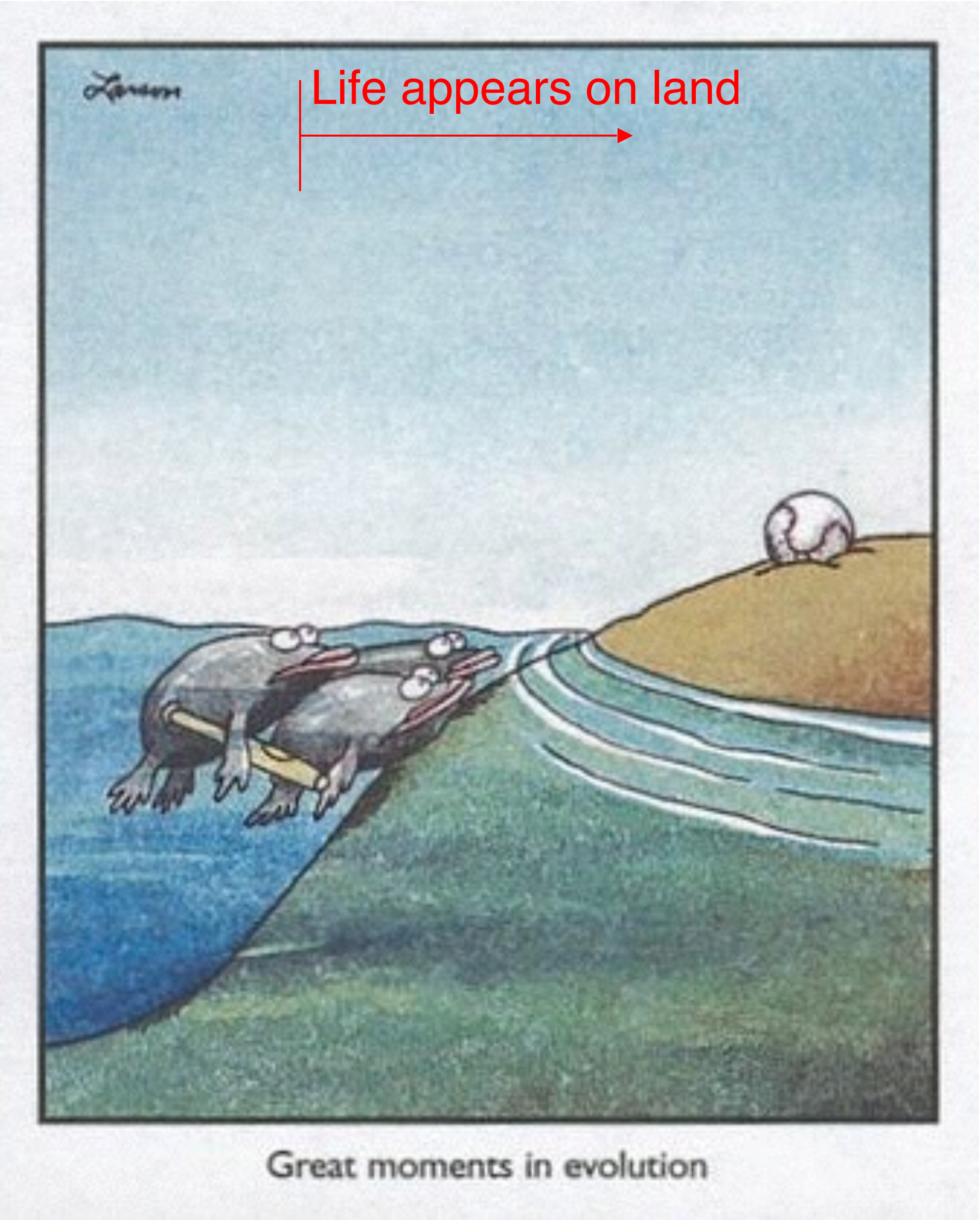
3.5 Gy B.P.

0.4 Gy B.P.

present

Evolution of oxygen and ozone over Earth's history





Life appears on land

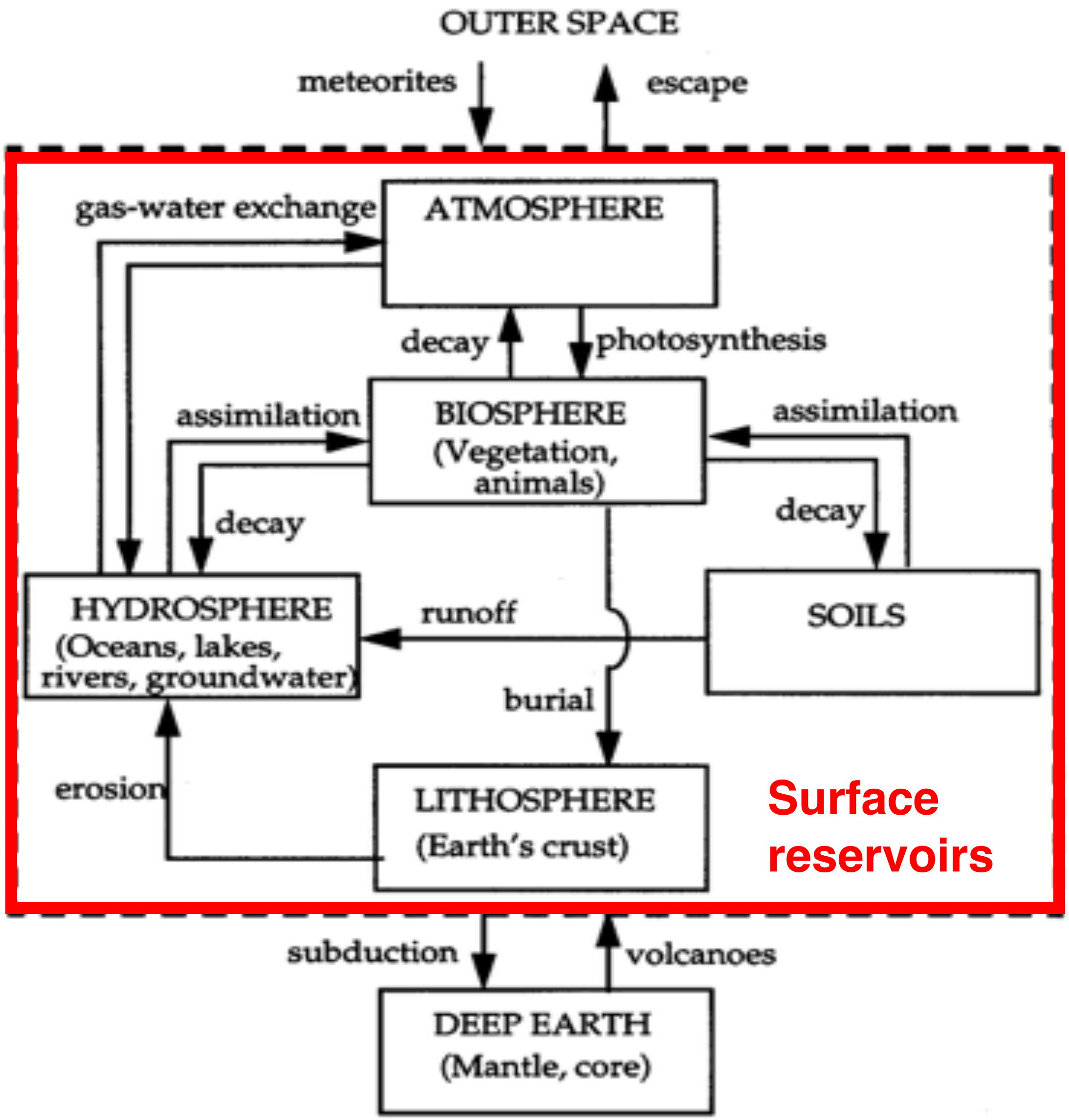
Great moments in evolution

Comparing the atmospheres of Earth and Venus

	Venus	Earth
Radius (km)	6100	6400
Surface pressure (atm)	91	1
CO_2 (mol/mol)	0.96	3×10^{-4}
N_2 (mol/mol)	3.4×10^{-2}	0.78
O_2 (mol/mol)	6.9×10^{-5}	0.21
H_2O (mol/mol)	3×10^{-3}	1×10^{-2}

BIOGEOCHEMICAL CYCLING OF ELEMENTS: examples of major processes

Physical exchange, redox chemistry, biochemistry are involved



Change in molecular form of an element by redox reactions

Redox reaction: oxidant + reductant → products

I want electrons! I want to get rid of electrons!

Let's do it!

An atom minimizes energy by filling lowest-energy orbitals in its outermost (valence) electron shell: this is done by acquiring or donating electrons through bonding

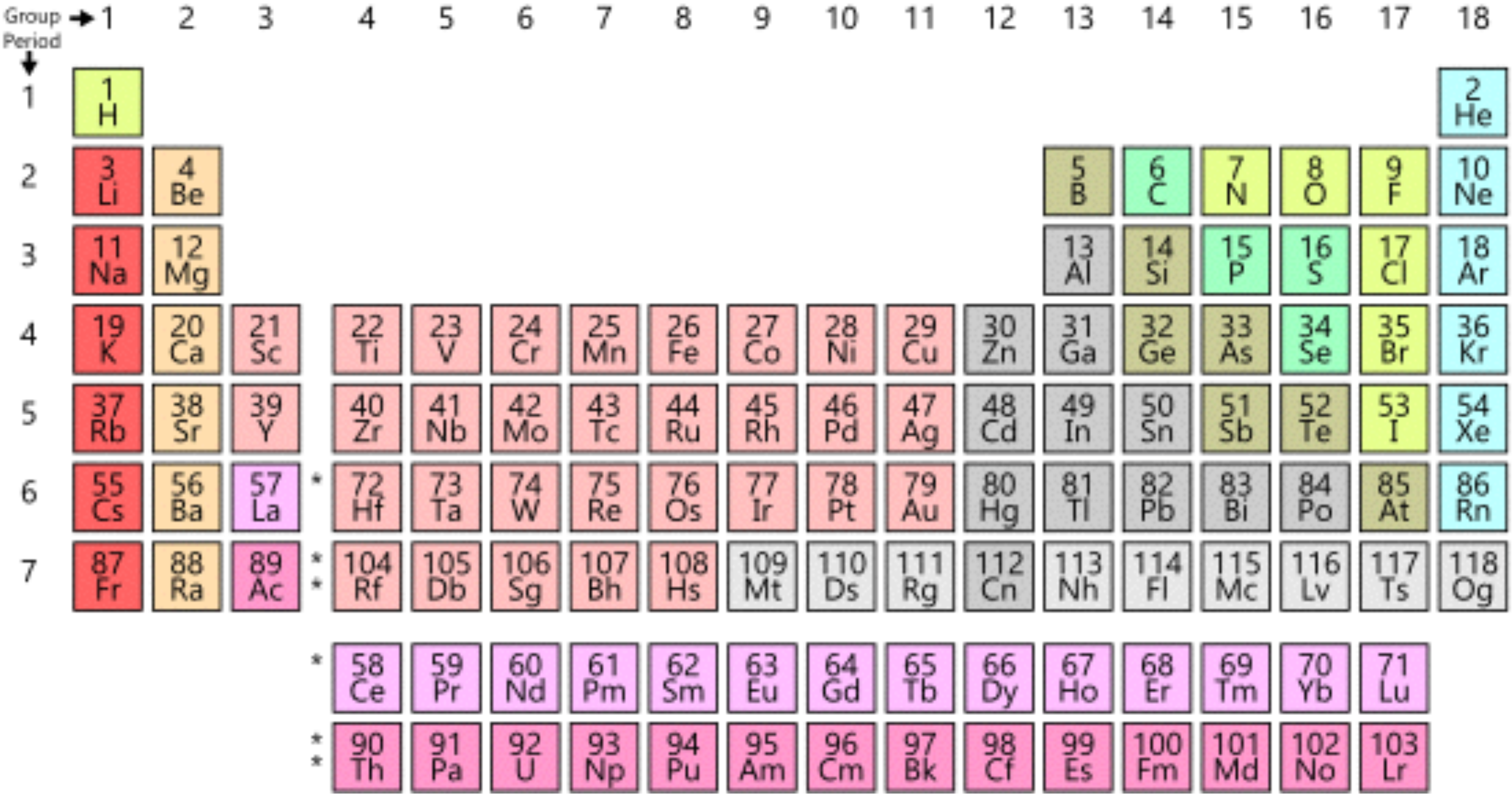
First valence shell has 2 electrons; second has 8; third has 18 (but 8 low-energy),…

In periodic table, atomic number gives number of electrons in neutral/unbound atom: this corresponds to oxidation state zero (0) for that element. Oxidation state becomes negative if atom acquires electrons, positive if it donates.

Some handy rules:

- A neutral molecule has total oxidation number 0
- Bound oxygen has oxidation state -2
- Bound hydrogen has oxidation state +1

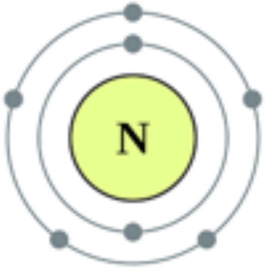
Periodic table of elements showing atomic numbers



Group → Period ↓	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	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
5	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
6	55 Cs	56 Ba	57 La	*	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
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				*	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	
				**	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	

OXIDATION STATES OF NITROGEN

N has 5 electrons in valence shell ⇨9 oxidation states from –3 to +5



Increasing oxidation number (nitrogen is oxidized)

→

-3	0	+1	+2	+3	+4	+5
NH_3 **Ammonia** NH_4^+ **Ammonium** $R_1N(R_2)R_3$ **Organic N**	N_2 **Dinitrogen**	N_2O **Nitrous oxide**	NO **Nitric oxide**	HONO **Nitrous acid** NO_2^- **Nitrite**	NO_2 **Nitrogen dioxide**	HNO_3 **Nitric acid** NO_3^- **Nitrate**

←

Decreasing oxidation number (nitrogen is reduced)

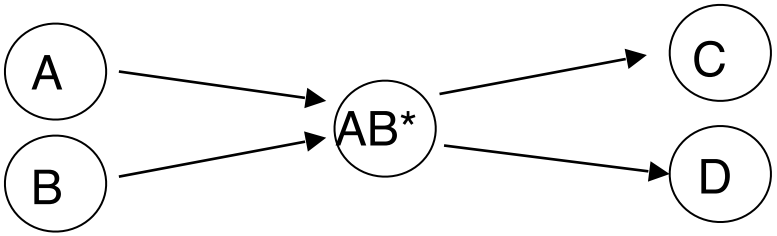
Questions

1. Although volcanoes don't emit O_2 they do emit a lot of oxygen (as H_2O and CO_2). Both H_2O and CO_2 photolyze in the upper atmosphere. Photolysis of H_2O eventually results in production of atmospheric O_2 and this is thought to be responsible for the presence of O_2 in the atmosphere before the onset of photosynthesis. However, photolysis of CO_2 does not result in production of O_2. Why this difference?

2. How many net molecules of O_2 are needed to oxidize N_2 to HNO_3?

Elementary vs. stoichiometric reactions

An **elementary reaction** is one that arises from the actual collision of reactants, from which the kinetics can be deduced:



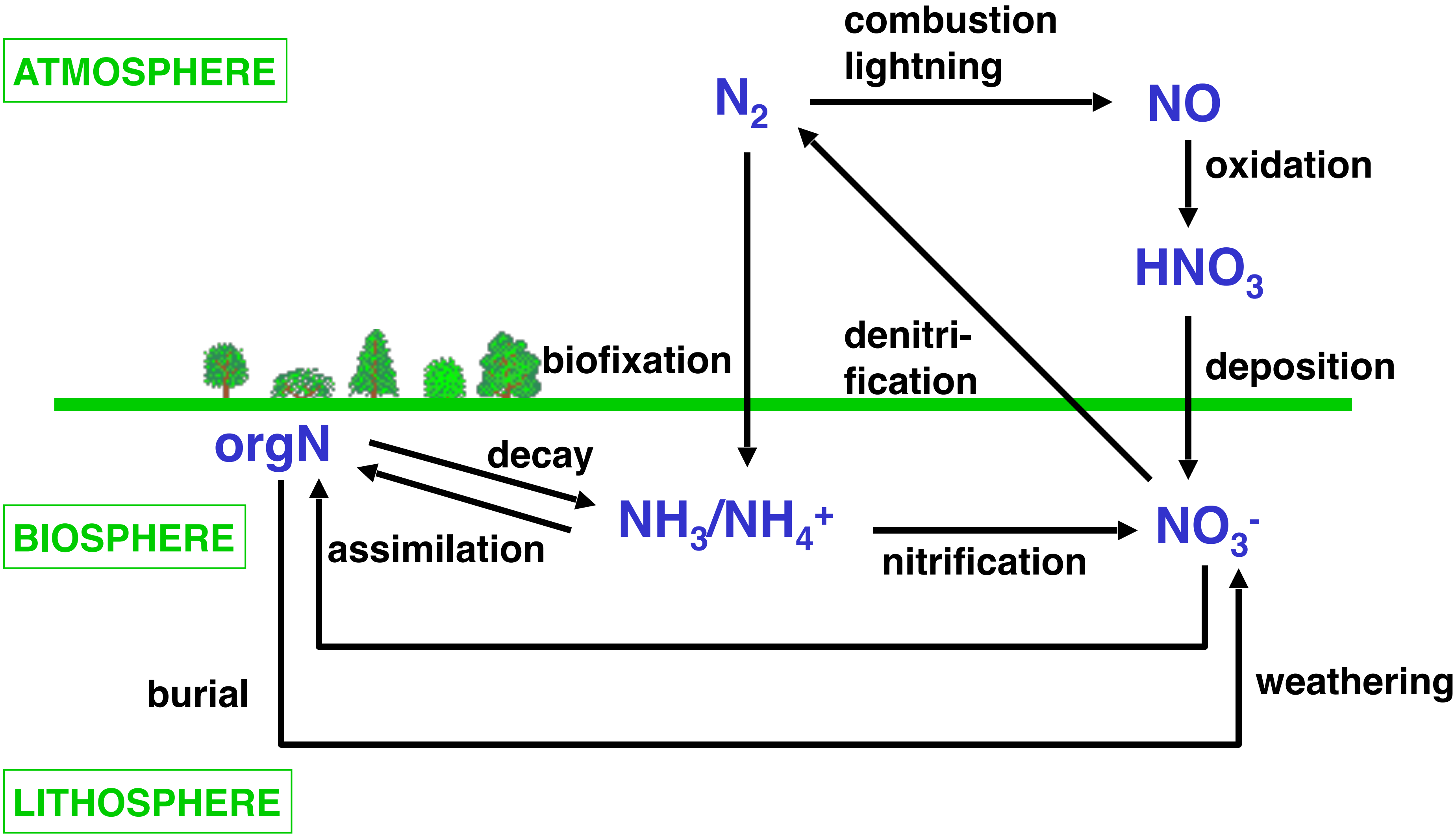
$$A + B \rightarrow C + D$$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} = k[A][B]$$

A **stoichiometric reaction** is one that describes the net outcome of a reaction sequence, without any information on kinetics or mechanism. For example, combustion of a hydrocarbon C_xH_y is described stoichiometrically by

$$C_xH_y + (x+y/4)\, O_2 \rightarrow x\, CO_2 + y/2\, H_2O$$

THE NITROGEN CYCLE: MAJOR PROCESSES



ATMOSPHERE

N_2

combustion
lightning

NO

oxidation

HNO_3

deposition

denitrification

biofixation

BIOSPHERE

orgN

decay

assimilation

NH_3/NH_4^+

nitrification

NO_3^-

burial

weathering

LITHOSPHERE

Ammonia formation by Haber-Bosch process (1909)

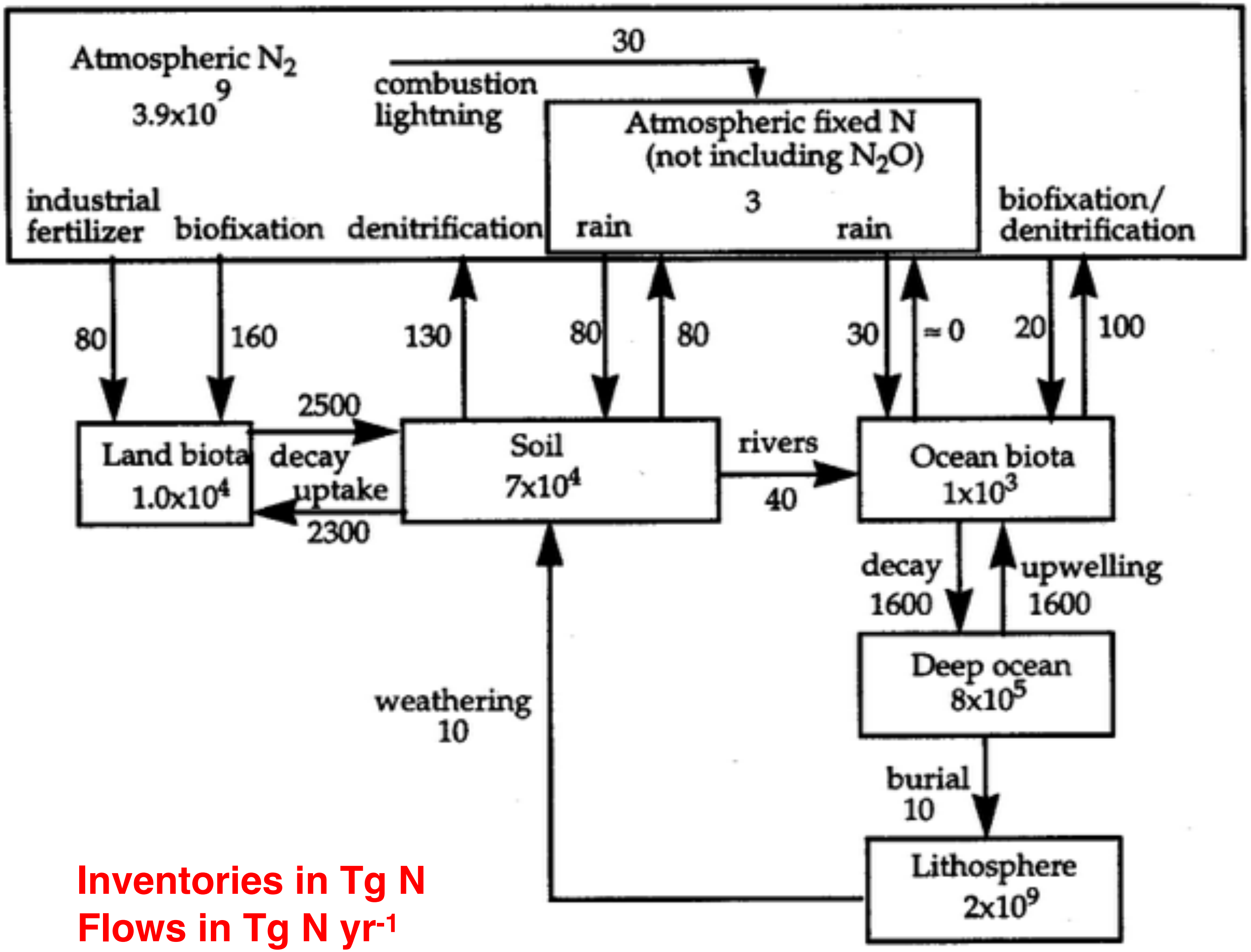
$$N_2 + 3H_2 \xrightarrow{\substack{\text{high } T,\ p \\ \text{metal catalyst}}} 2NH_3$$

enabled 20th century population growth through fertilizer production

Fritz Haber

Carl Bosch

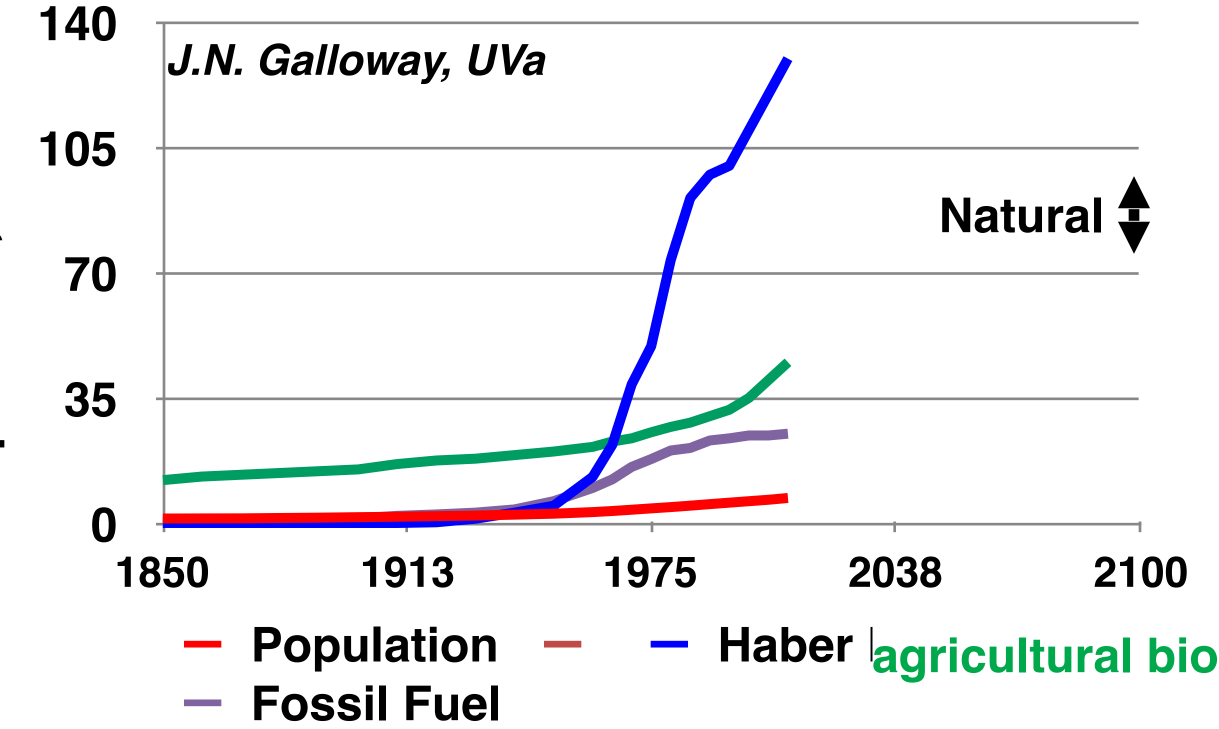
BOX MODEL OF THE NITROGEN CYCLE



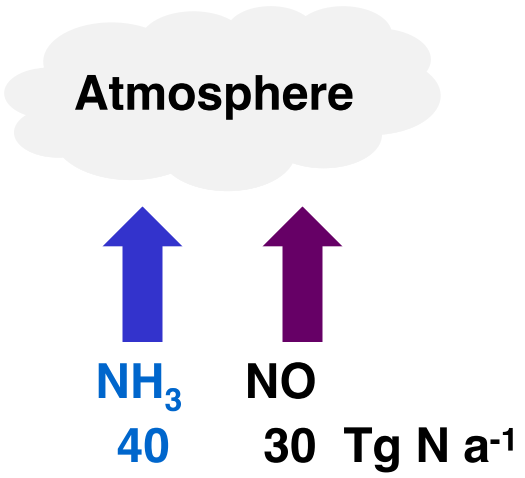
Inventories in Tg N
Flows in Tg N yr^{-1}

Global human perturbation to nitrogen cycle

Global anthropogenic N fixation now exceeds natural:



agricultural biofixation ▬ **fossil fuel**

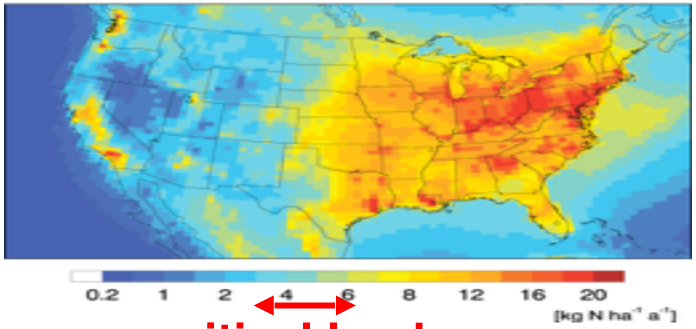

Atmosphere

NH_3 40

NO 30 Tg N a^{-1}

Resulting N deposition (NH_4^+, NO_3^-) modifies ecosystem function, C storage

Annual N deposition



critical load

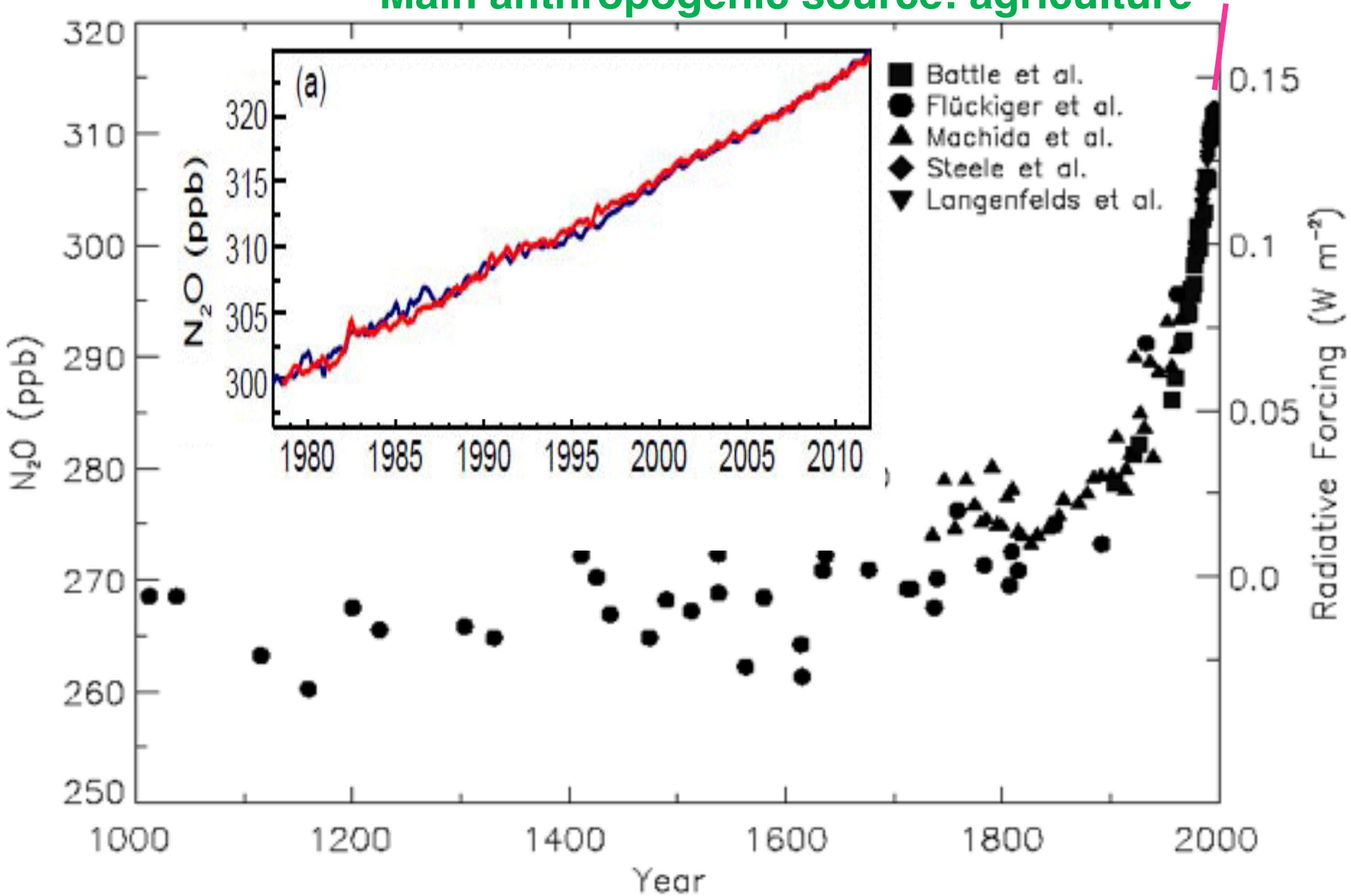
Zhang et al. [2012]

N_2O: LOW-YIELD PRODUCT OF BACTERIAL NITRIFICATION AND DENITRIFICATION

Important as

- source of NO_x radicals in stratosphere
- greenhouse gas

Main anthropogenic source: agriculture



IPCC [2014]

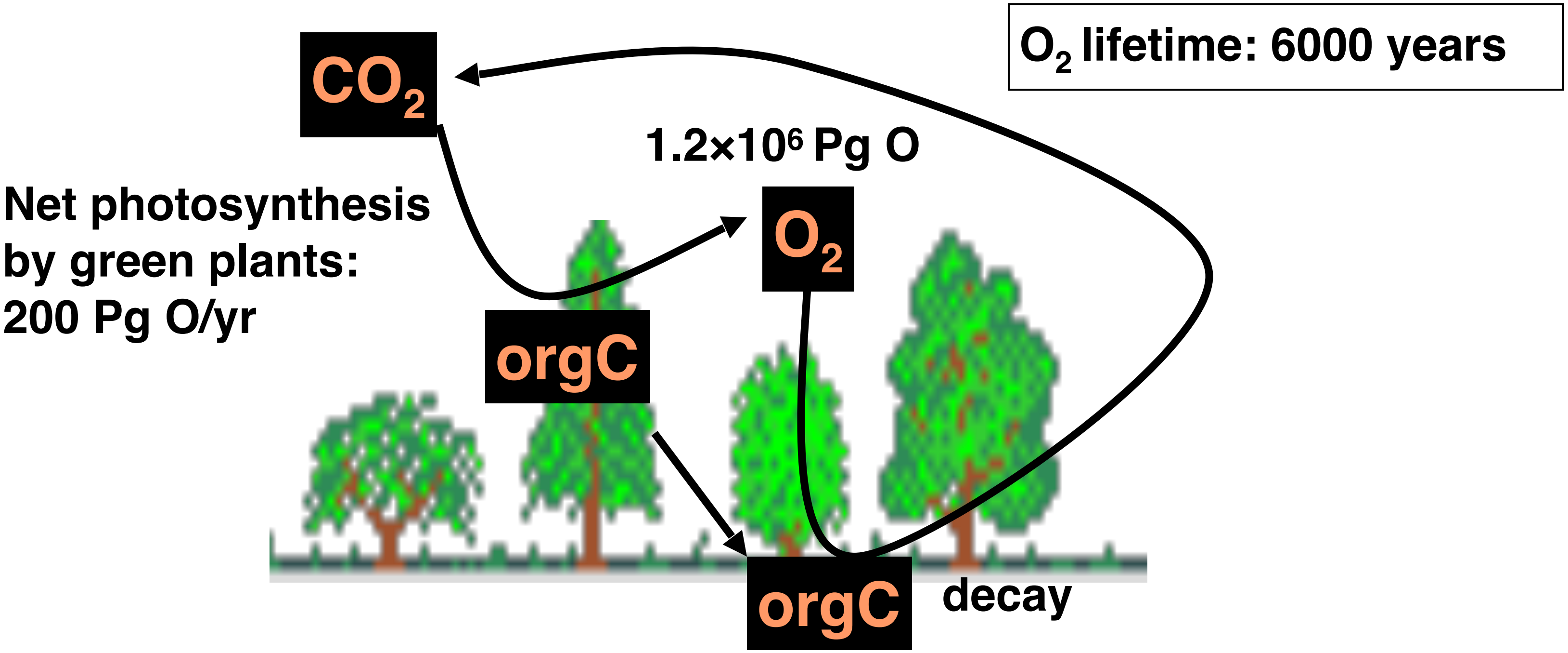
FAST OXYGEN CYCLE: ATMOSPHERE-BIOSPHERE

- Source of O_2: photosynthesis

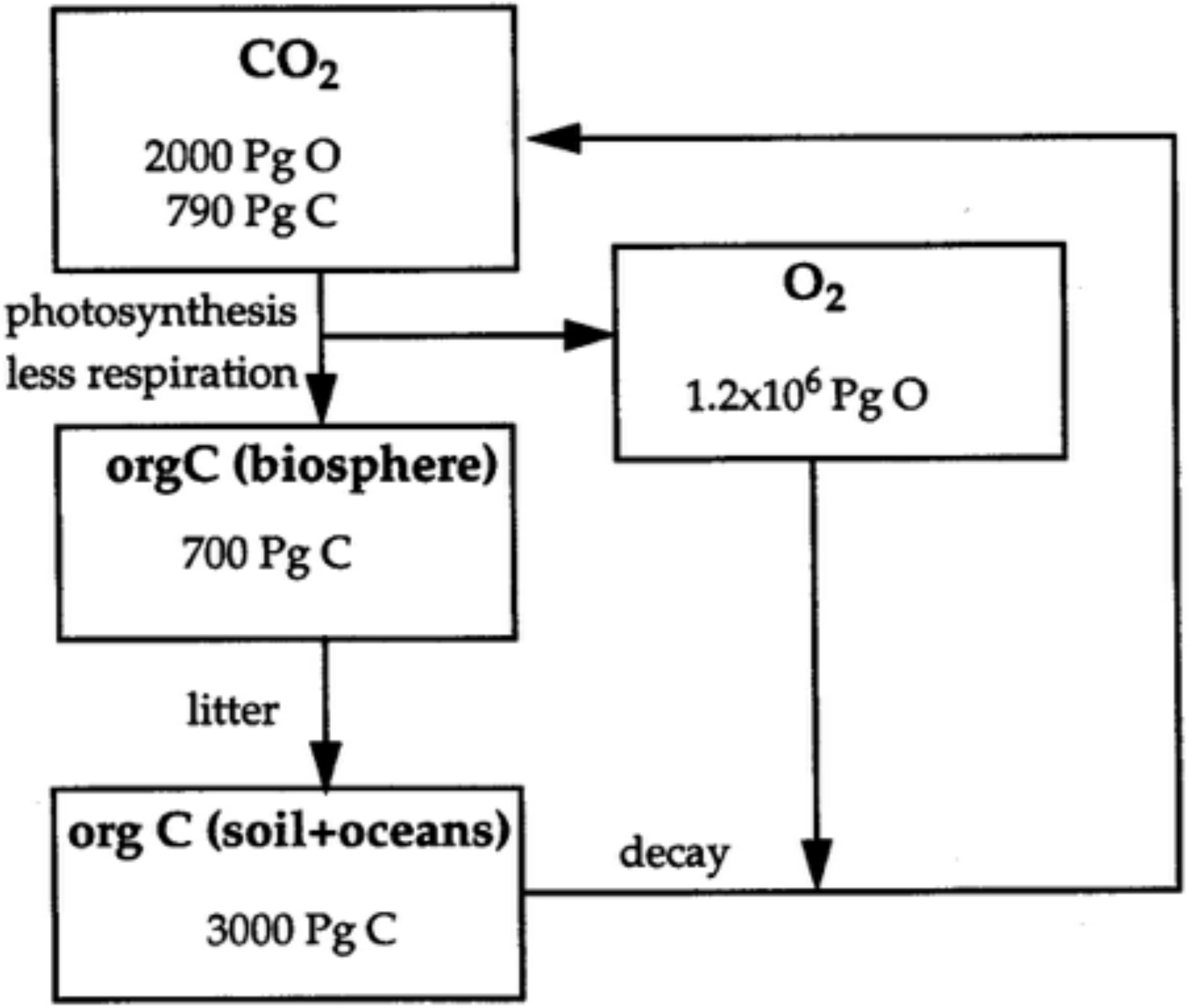
$$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2$$

- Sink: respiration/decay

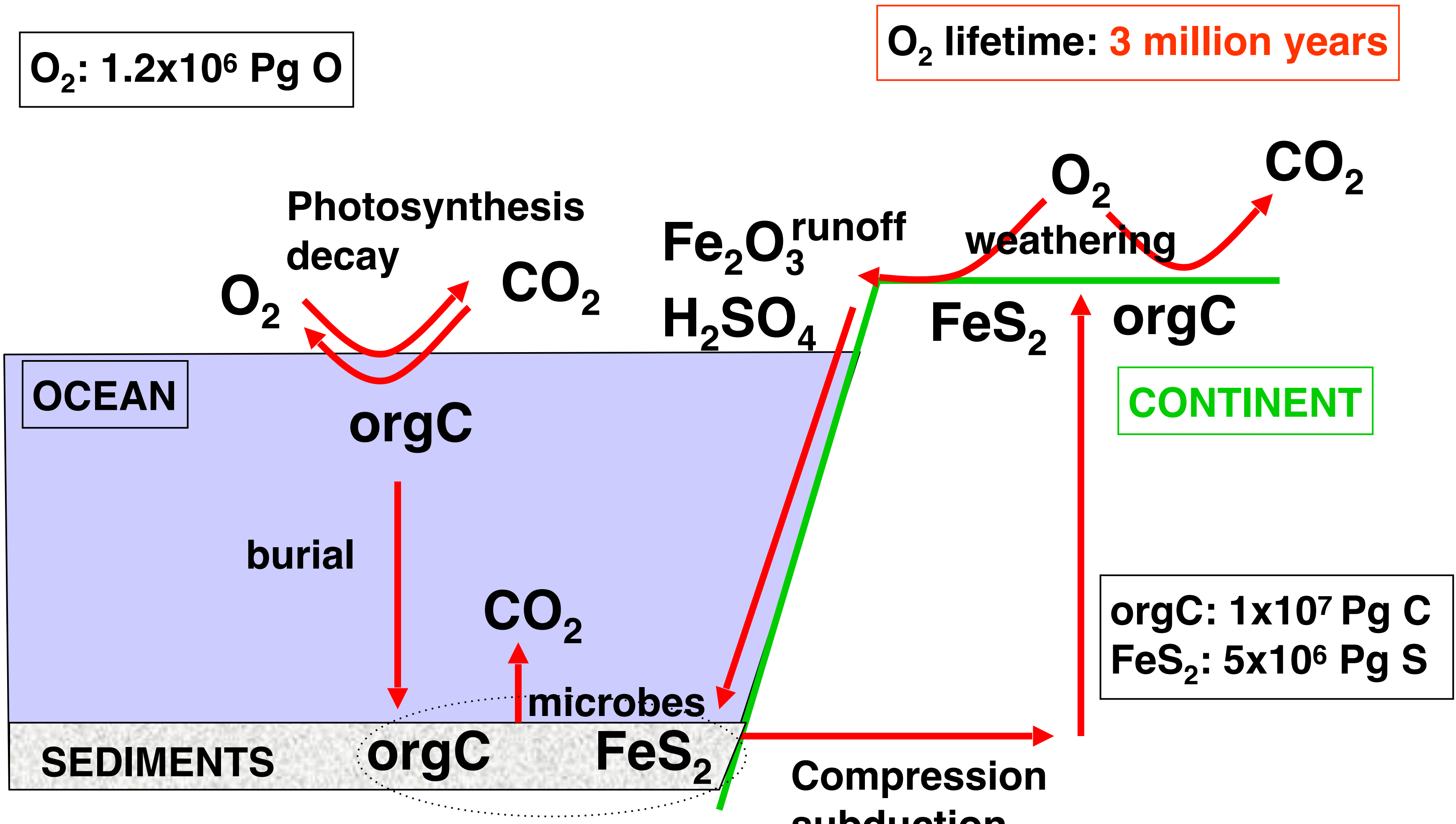
$$(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O$$



…but abundance of organic carbon in biosphere/soil/ocean reservoirs is too small to control atmospheric O_2 levels



SLOW OXYGEN CYCLE: ATMOSPHERE-LITHOSPHERE



O_2: 1.2×10^6 Pg O

O_2 lifetime: 3 million years

Photosynthesis

decay

O_2

CO_2

OCEAN

orgC

burial

CO_2

microbes

SEDIMENTS

orgC

FeS_2

Fe_2O_3

H_2SO_4

runoff

O_2

weathering

CO_2

FeS_2

orgC

CONTINENT

orgC: 1×10^7 Pg C

FeS_2: 5×10^6 Pg S

Compression

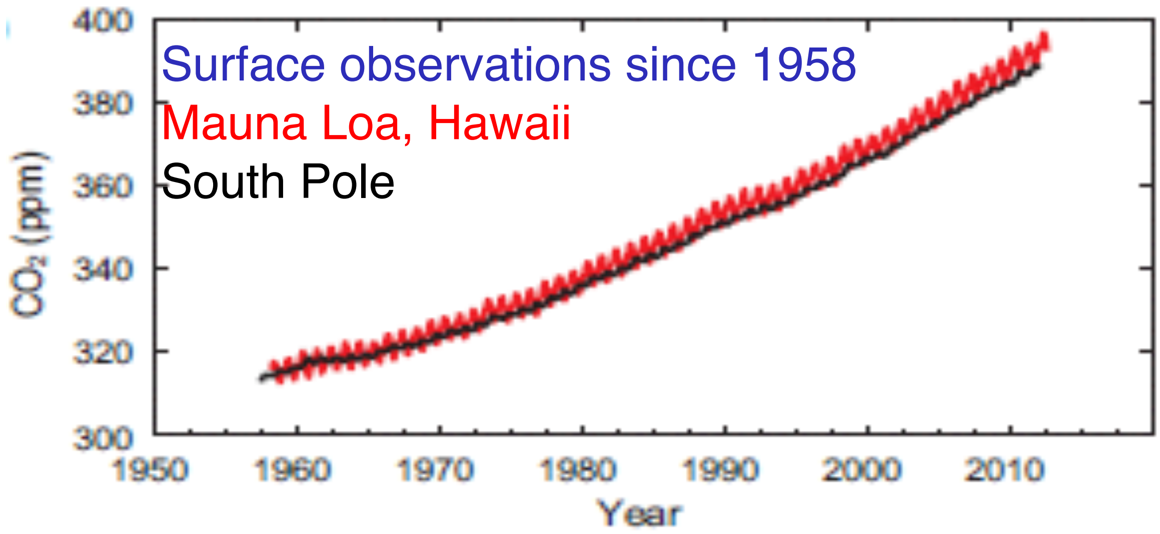
subduction

Questions

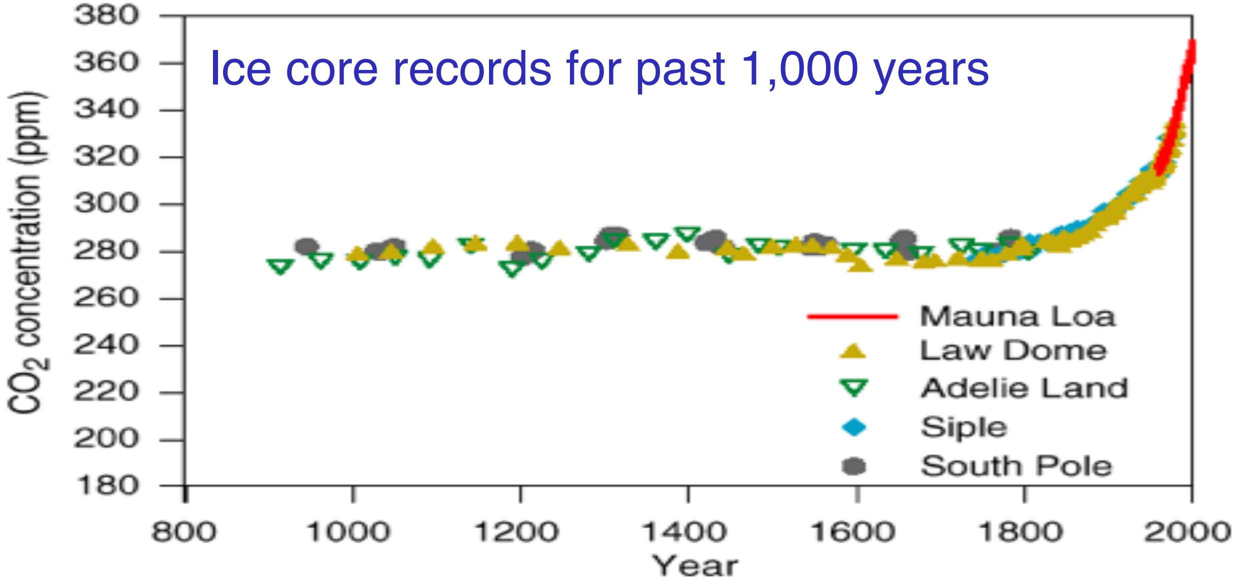
1. Denitrification seems at first glance to be a terrible waste for the biosphere, jettisoning precious fixed nitrogen back to the atmospheric N_2 reservoir. In fact, denitrification is essential for maintaining life in the interior of continents. Why?

2. Would shutting down of photosynthesis eventually deplete atmospheric O_2?

Increase in atmospheric CO_2 from fossil fuel combustion



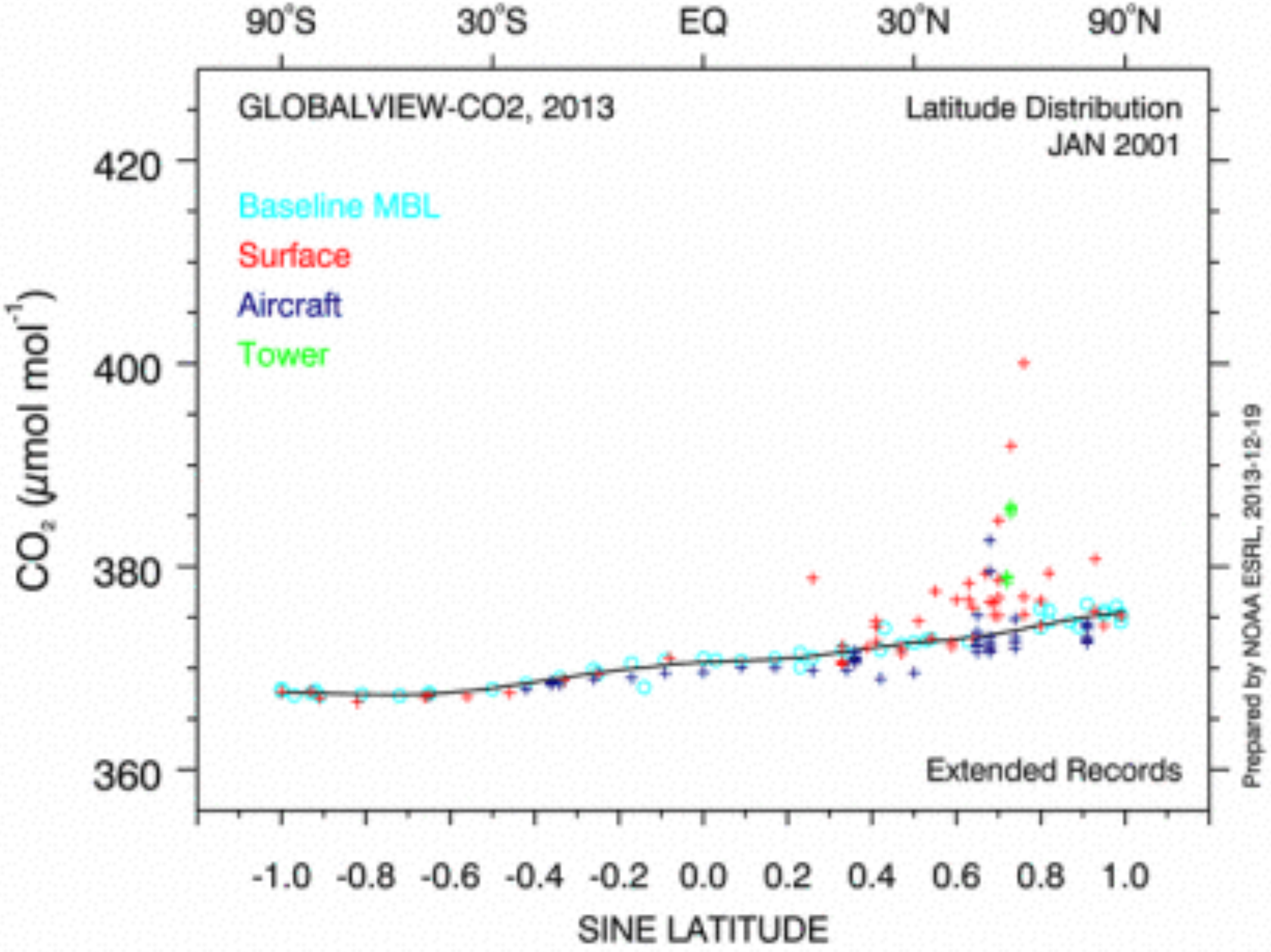
2017: 405 ppm



10 billion tons of carbon
per year (2017)

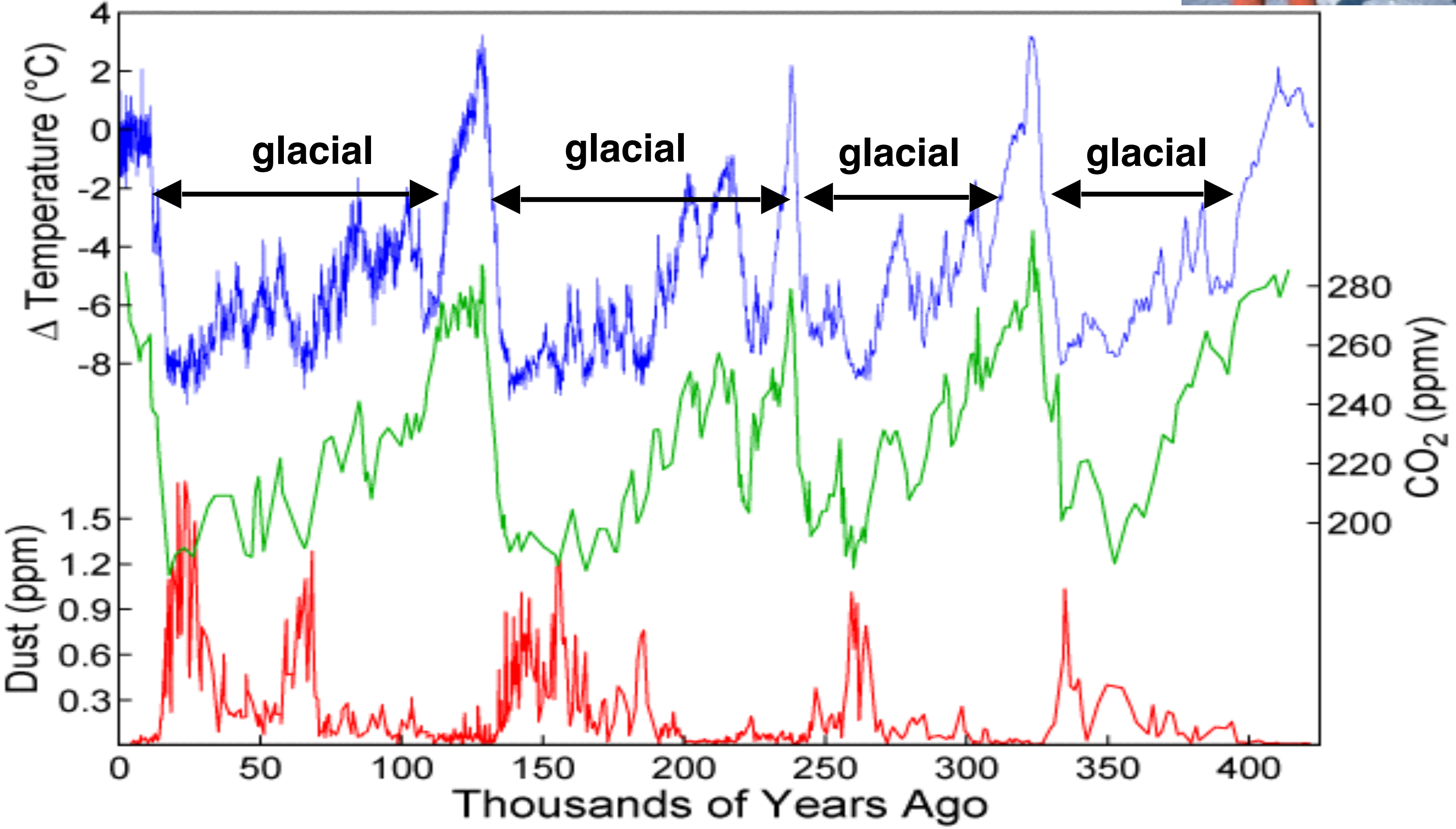
IPCC [2007, 2014]

Rising atmospheric CO_2 vs. latitude, 2001-2012



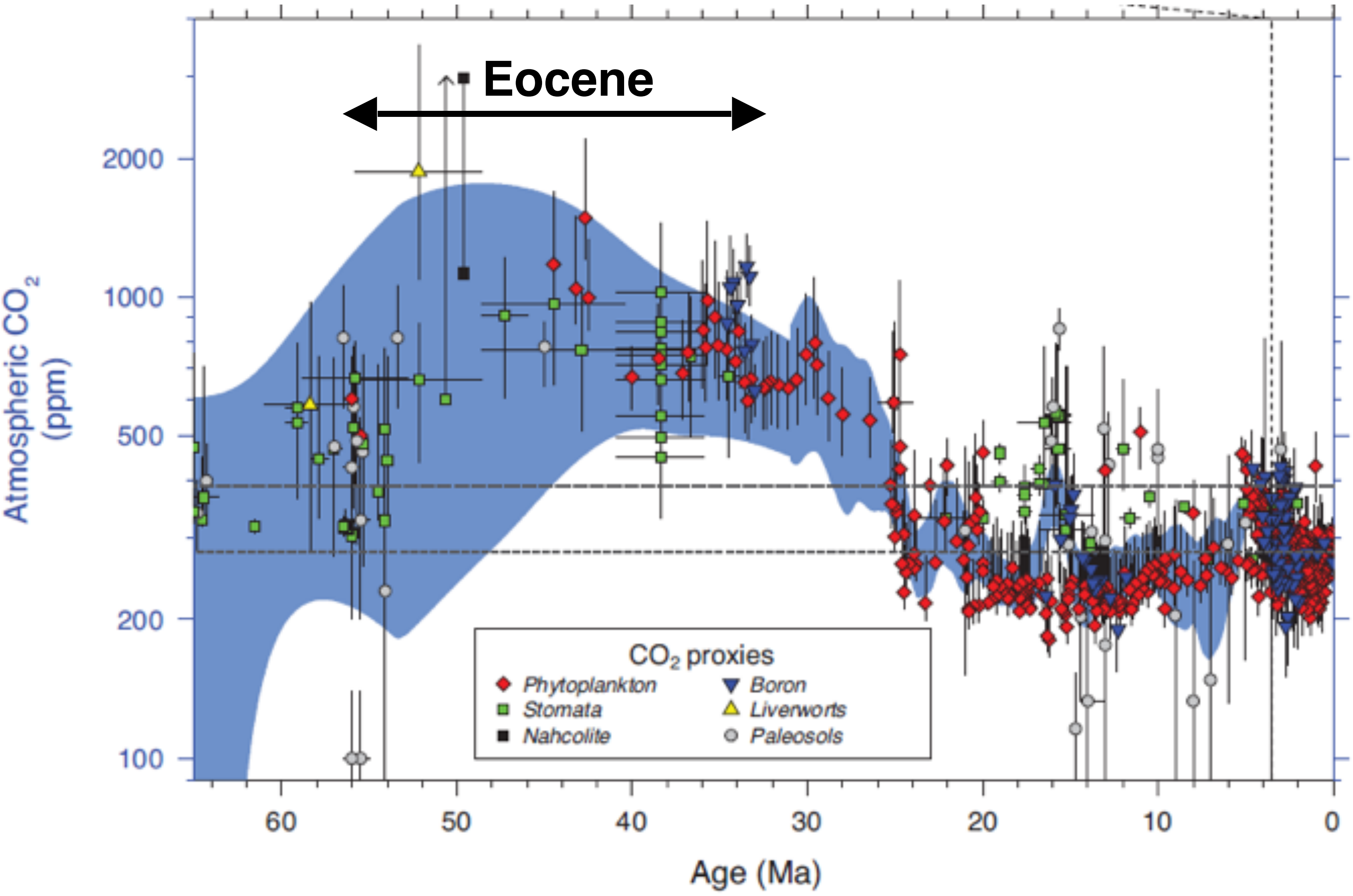
https://www.esrl.noaa.gov/gmd/ccgg/globalview/

Temperature and CO_2 records in Antarctic ice cores



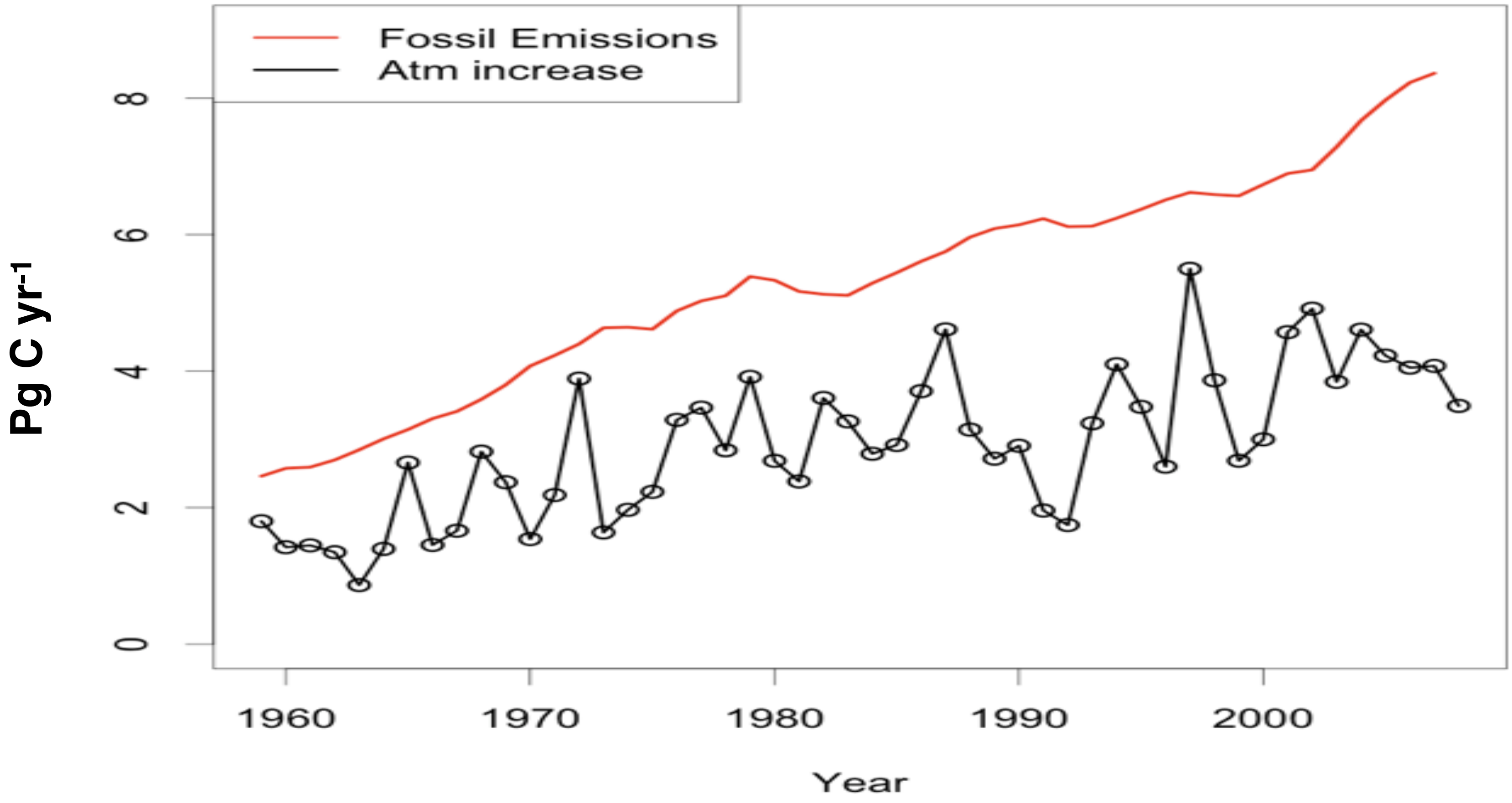
Vostok ice core (East Antarctica)

CO_2 over the last 60 million years



IPCC [2014]

INTERANNUAL TREND IN CO_2 INCREASE



On average, only 60% of emitted CO_2 remains in the atmosphere – but there is large interannual variability in this fraction

Equilibrium constants

If we have a forward reaction $A + B \rightarrow C + D$ (rate constant k_f)

then we must have the backward reaction $C + D \rightarrow A + B$ (rate constant k_b)

If the backward reaction is negligible then the forward reaction is said *irreversible*

If the backward reaction is significant then the forward reaction is said *reversible.*

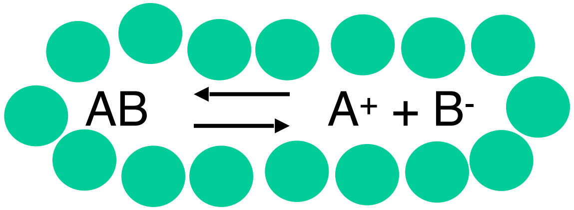
If the backward reaction is fast then the species may be in *equilibrium*:

$$A + B \leftrightarrows C + D \qquad \frac{d[A]}{dt} = k_b[C][D] - k_f[A][B] = 0 \Rightarrow \frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} = K$$

equilibrium constant

Ionic dissociation reactions in water are fast and best described by equilibrium constants:

$$AB \leftrightarrows A^+ + B^-$$



water molecules: “solvent cage”

$$K = \frac{[A^+][B^-]}{[AB]}$$

UPTAKE OF CO_2 BY THE OCEANS

ATMOSPHERE

$CO_2(g)$

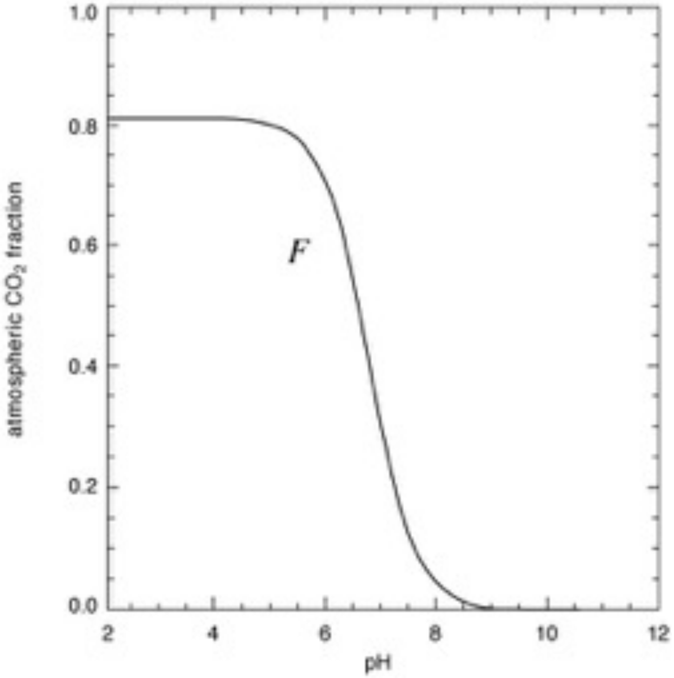
$\rightleftarrows$ $K_H = 3\times10^{-2}$ M atm^{-1}

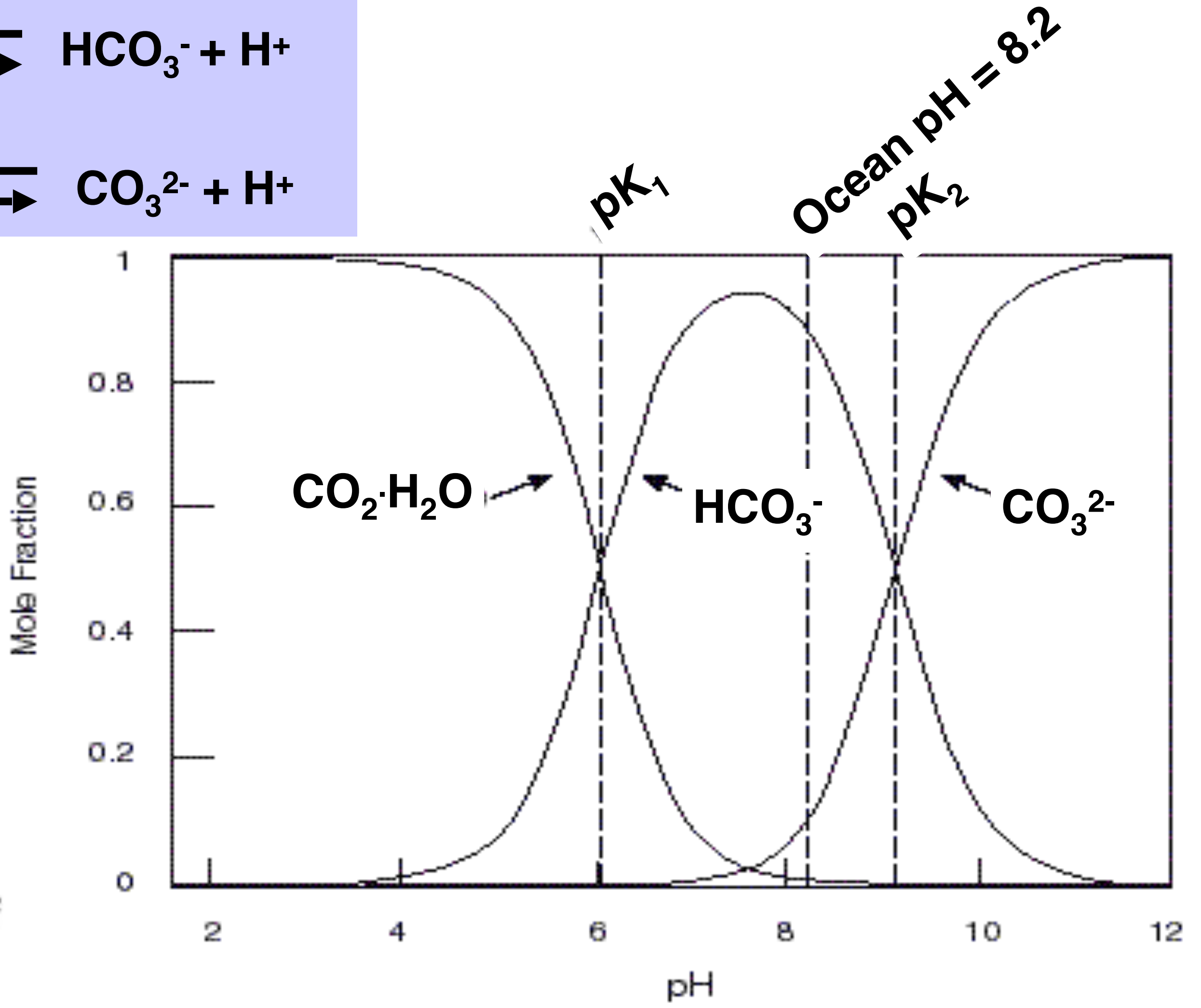
OCEAN

$CO_2{\cdot}H_2O$

$K_1 = 9\times10^{-7}$ M $\quad CO_2{\cdot}H_2O \rightleftarrows HCO_3^- + H^+$

$K_2 = 7\times10^{-10}$ M $\quad HCO_3^- \rightleftarrows CO_3^{2-} + H^+$





EQUILIBRIUM PARTITIONING OF CO_2 BETWEEN ATMOSPHERE AND GLOBAL OCEAN

Equilibrium for present-day ocean:

$$F = \frac{N_{CO2}(g)}{N_{CO2}(g) + N_{CO2}(aq)} = \frac{1}{1 + \frac{V_{oc} P K_{\mathrm{H}}}{\mathrm{N}_a}\left(1 + \frac{K_1}{[\mathrm{H}^+]} + \frac{K_1 K_2}{[\mathrm{H}^+]^2}\right)} = 0.03$$

⇨ **only 3% of total inorganic carbon is currently in the atmosphere**

But $CO_2(g)$ ↗ ⇨ $[H^+]$ ↗ ⇨ F ↗

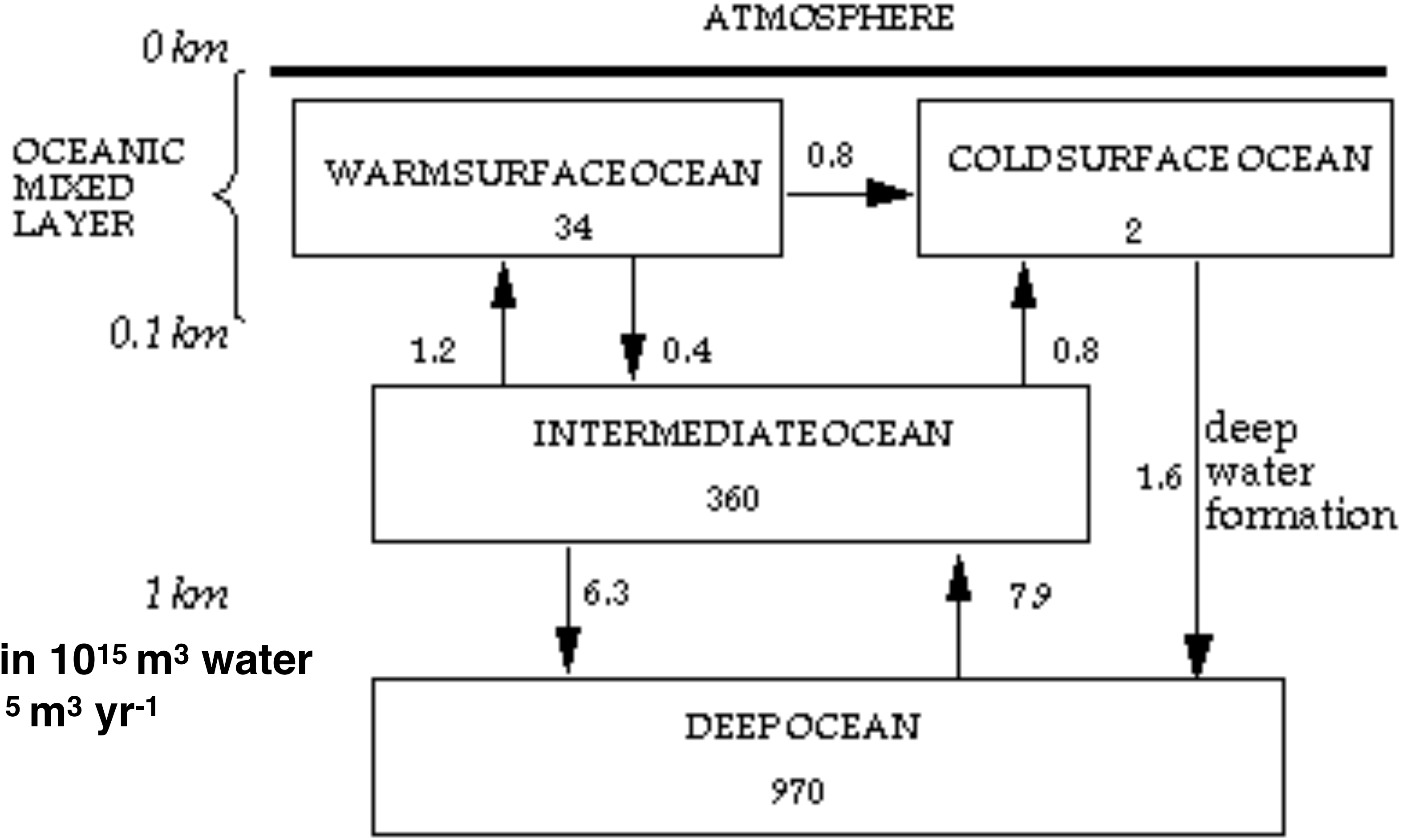
… positive feedback to increasing CO_2

Pose problem differently: how does a CO_2 addition *dN* partition between the atmosphere and ocean at equilibrium (whole ocean)?

$$f = \frac{dN_{CO2}(g)}{dN_{CO2}(g) + dN_{CO2}(aq)} = \frac{1}{1 + \frac{V_{oc} P K_{\mathrm{H}} K_1 K_2}{N_a \beta \left[\mathrm{H}^+\right]^2}} = 0.28$$

⇨ **28% of added CO_2 remains in atmosphere!**

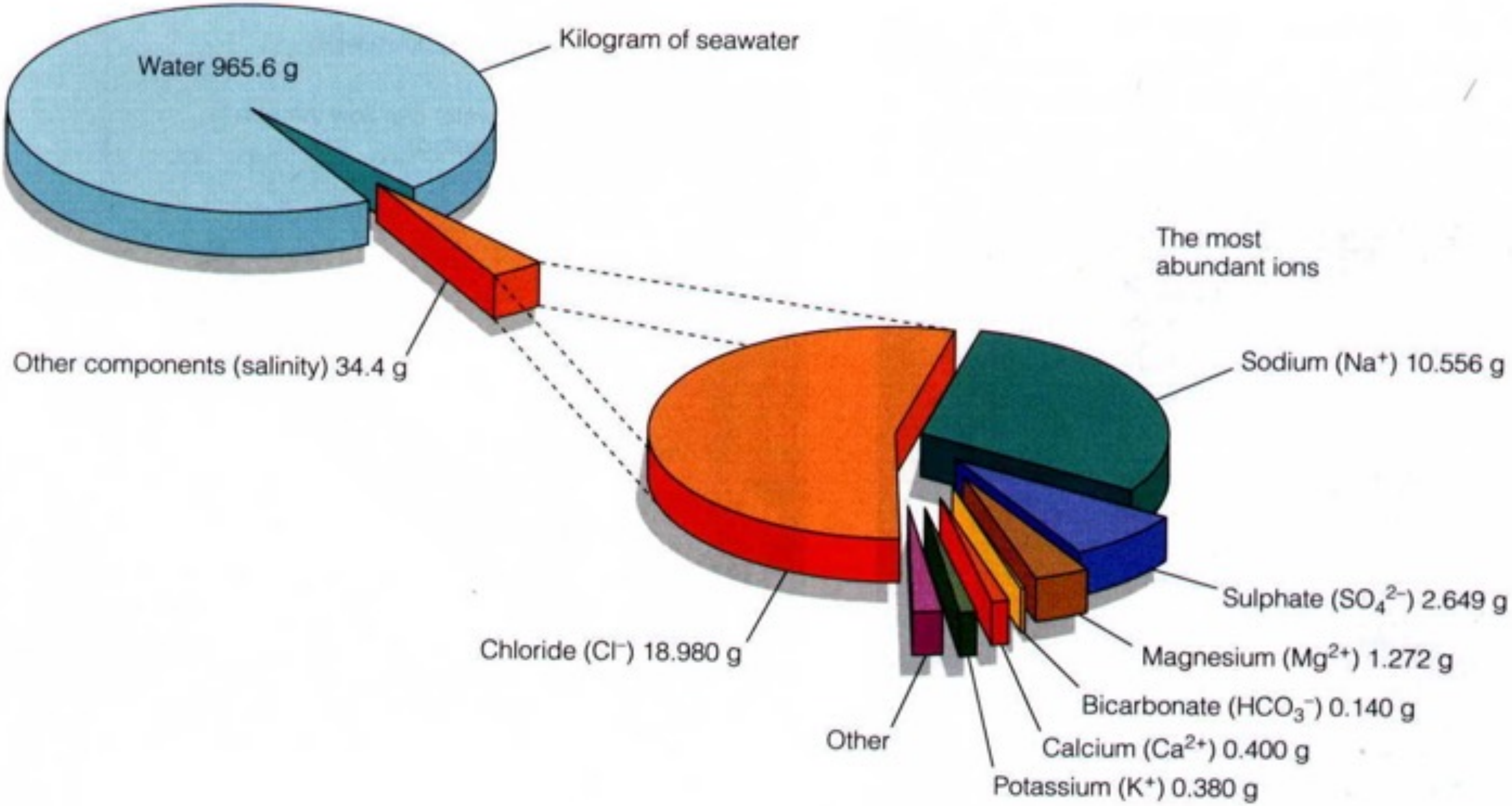
ADDITIONAL LIMITATION OF CO_2 UPTAKE: SLOW OCEAN TURNOVER (~ 200 years)



Inventories in 10^{15} m^3 water
Flows in 10^{15} m^3 yr^{-1}

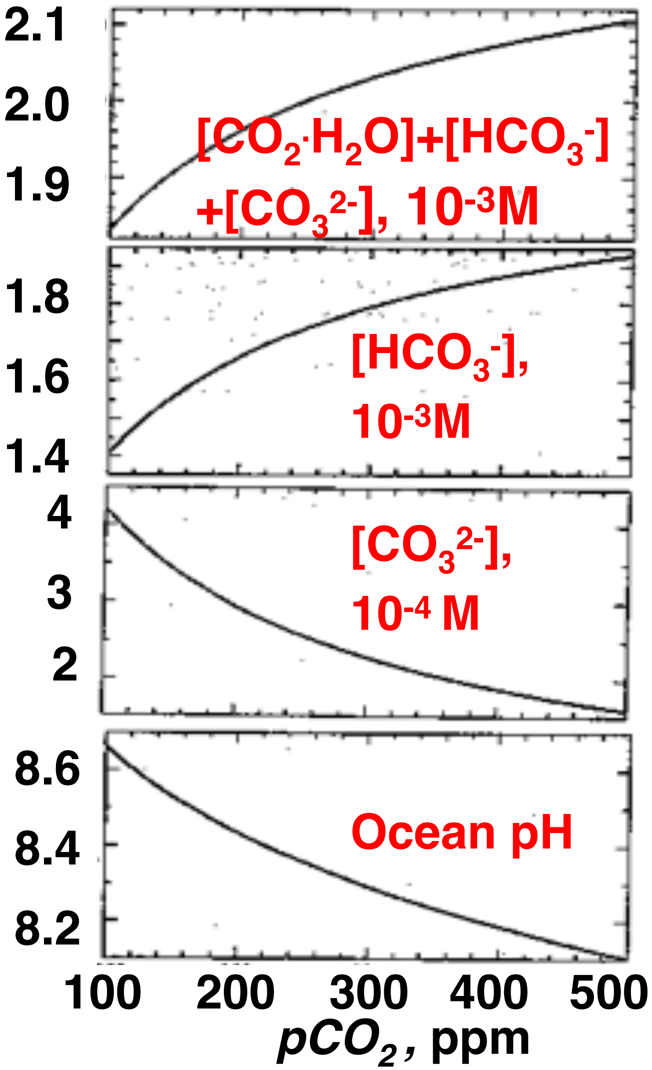
Uptake by oceanic mixed layer only ($V_{OC} = 3.6\times10^{16}$ m^3) would give $f = 0.94$ (94% of added CO_2 remains in atmosphere)

MEAN COMPOSITION OF SEAWATER



LIMIT ON OCEAN UPTAKE OF CO_2: CONSERVATION OF ALKALINITY

Equilibrium calculation for [Alk] = 2.3×10^{-3} M



Charge balance in the ocean:

$[HCO_3^-] + 2[CO_3^{2-}] = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] - [Cl^-] – 2[SO_4^{2-}] – [Br^-]$

The *alkalinity* [Alk] ≈ $[HCO_3^-] + 2[CO_3^{2-}]$ = 2.3×10^{-3}M is the excess base relative to the CO_2-H_2O system

It is <u>conserved</u> upon addition of CO_2

⇨uptake of CO_2 is limited by the existing supply of CO_3^{2-}:

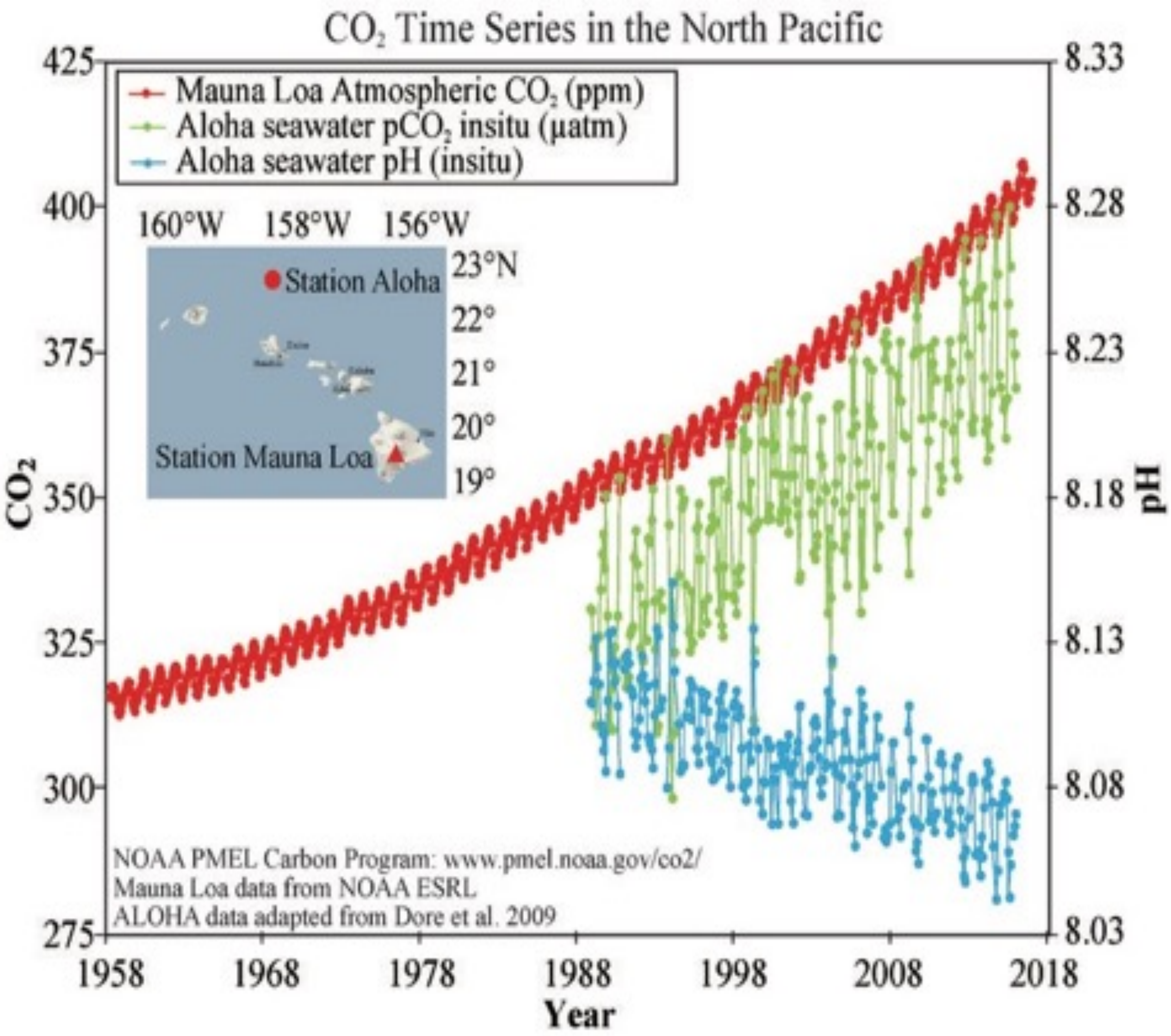
$$CO_{2(g)} + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^-$$

Increasing Alk requires dissolution of sediments:

$$CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-}$$

…which takes place over a time scale of thousands of years

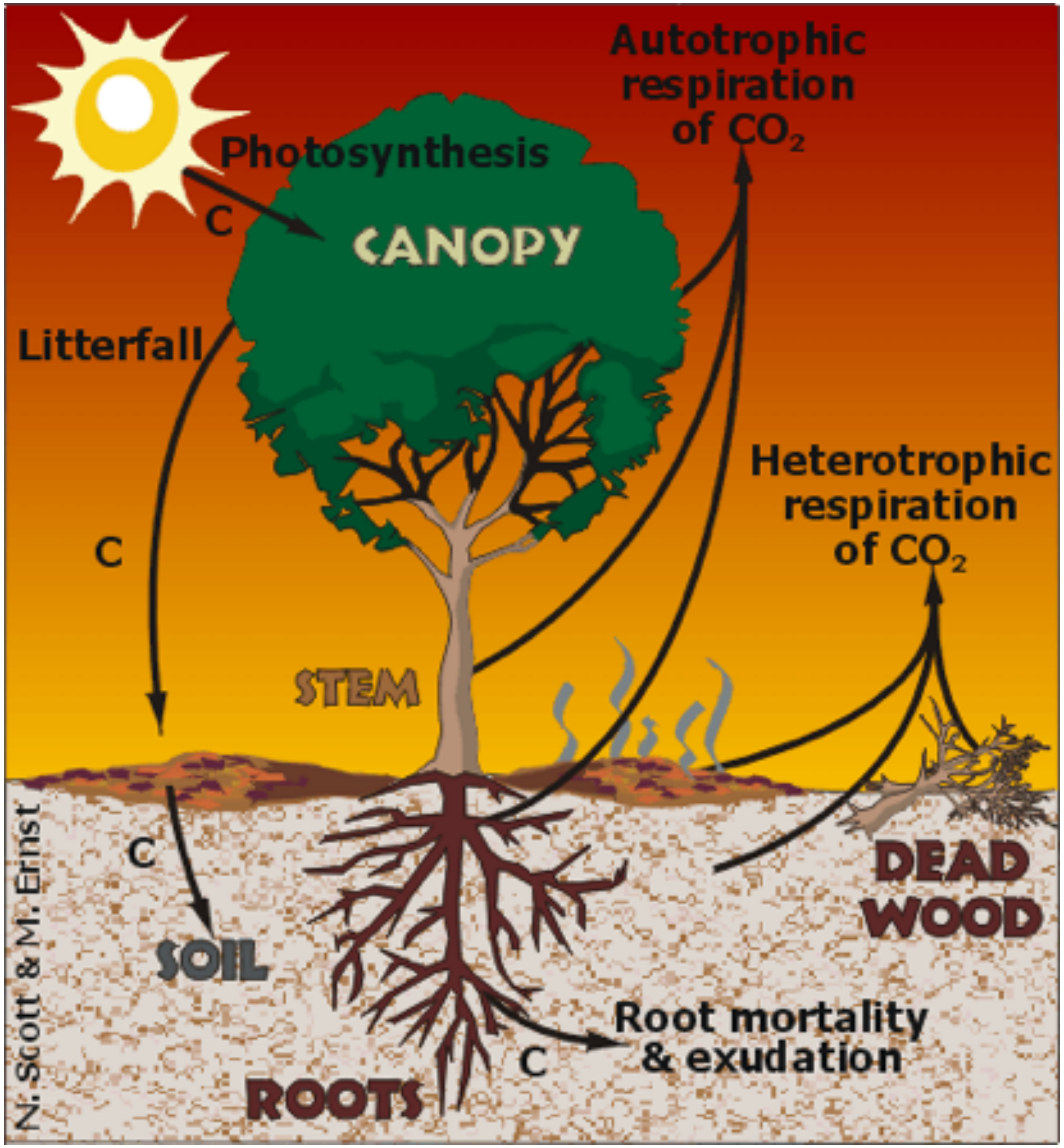
Observed ocean acidification



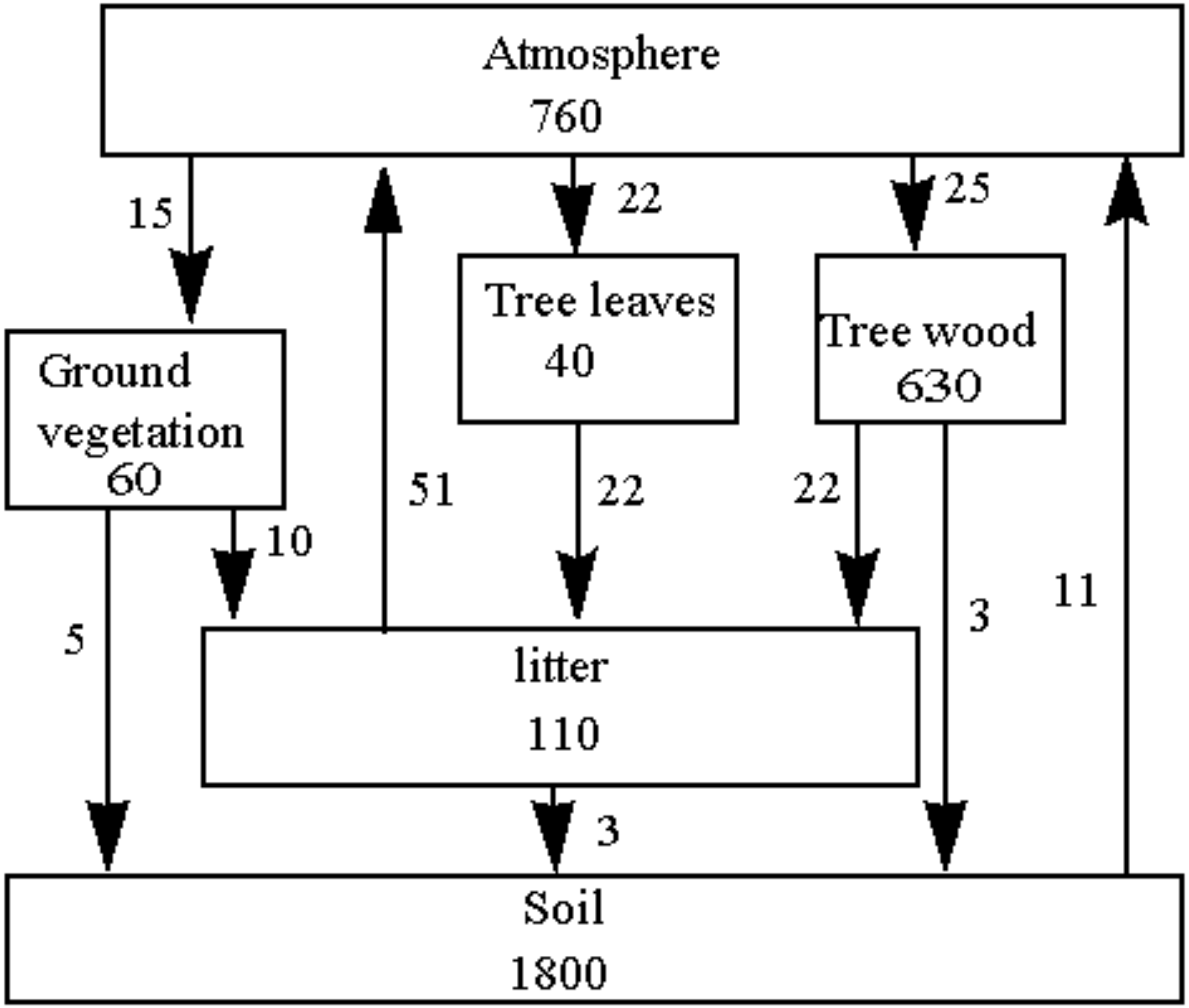
NOAA PMEL Carbon Program: www.pmel.noaa.gov/co2/
Mauna Loa data from NOAA ESRL
ALOHA data adapted from Dore et al. 2009

Data: Mauna Loa (ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_mm_mlo.txt) ALOHA (http://hahana.soest.hawaii.edu/hot/products/HOT_surface_CO2.txt)
Ref: J.E. Dore et al, 2009. Physical and biogeochemical modulation of ocean acidification in the central North Pacific. *Proc Natl Acad Sci USA* **106**:12235-12240.

LAND-ATMOSPHERE CARBON CYCLING: MAJOR PROCESSES

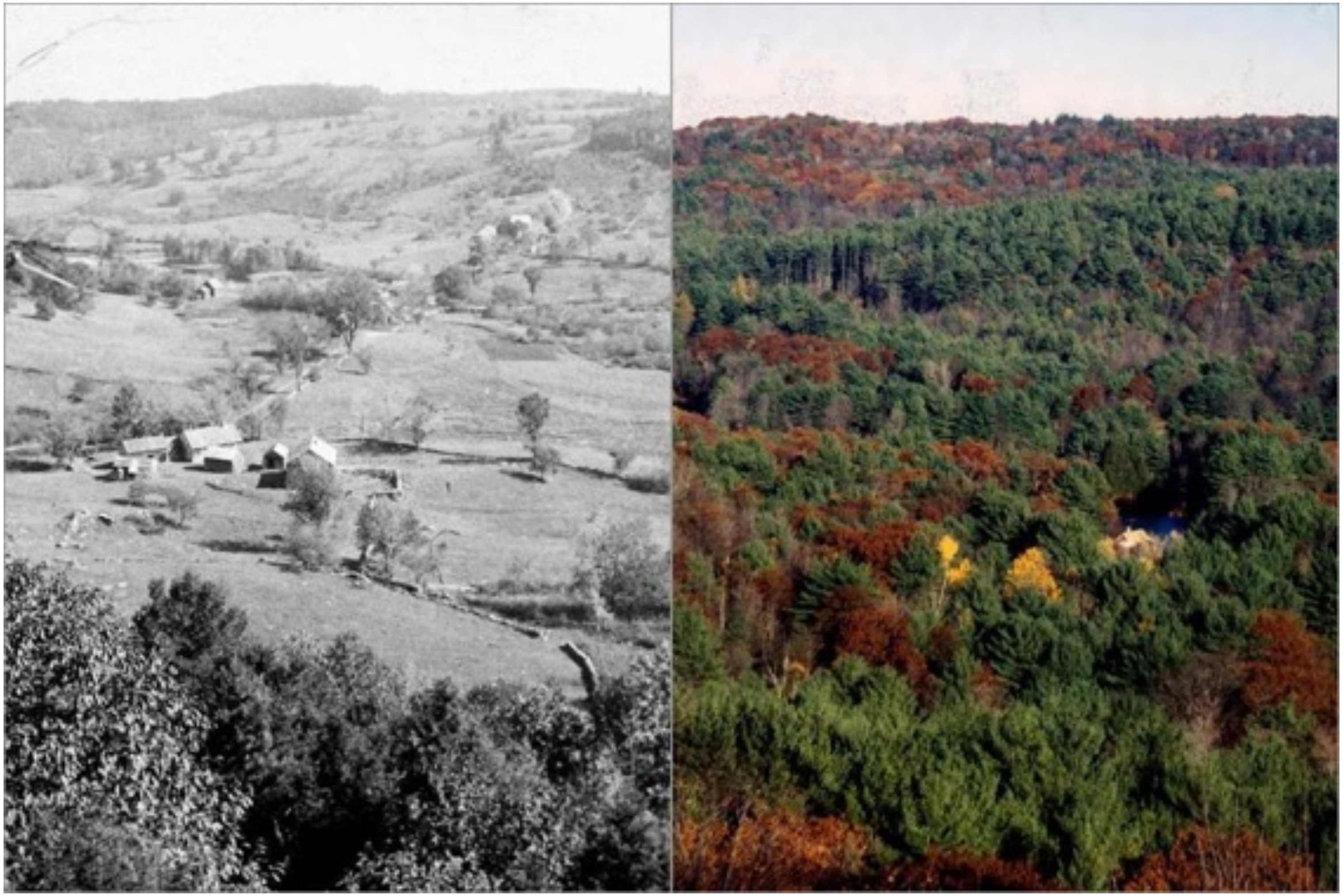


Land-atmosphere global carbon cycling

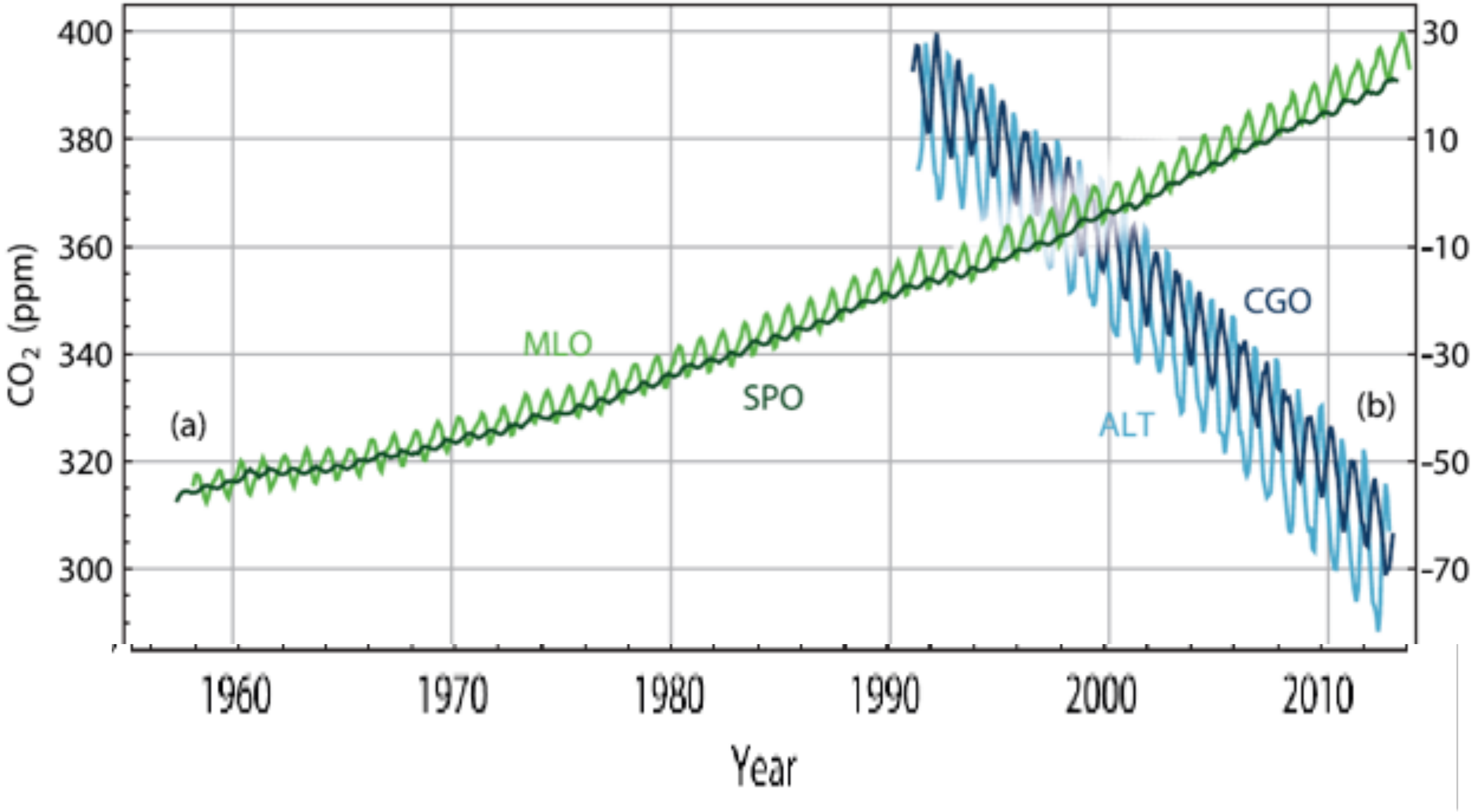


Inventories in PgC
Flows in PgC a^{-1}

Reforestation in action:
Harvard Forest in Petersham, central Mass. – then and now

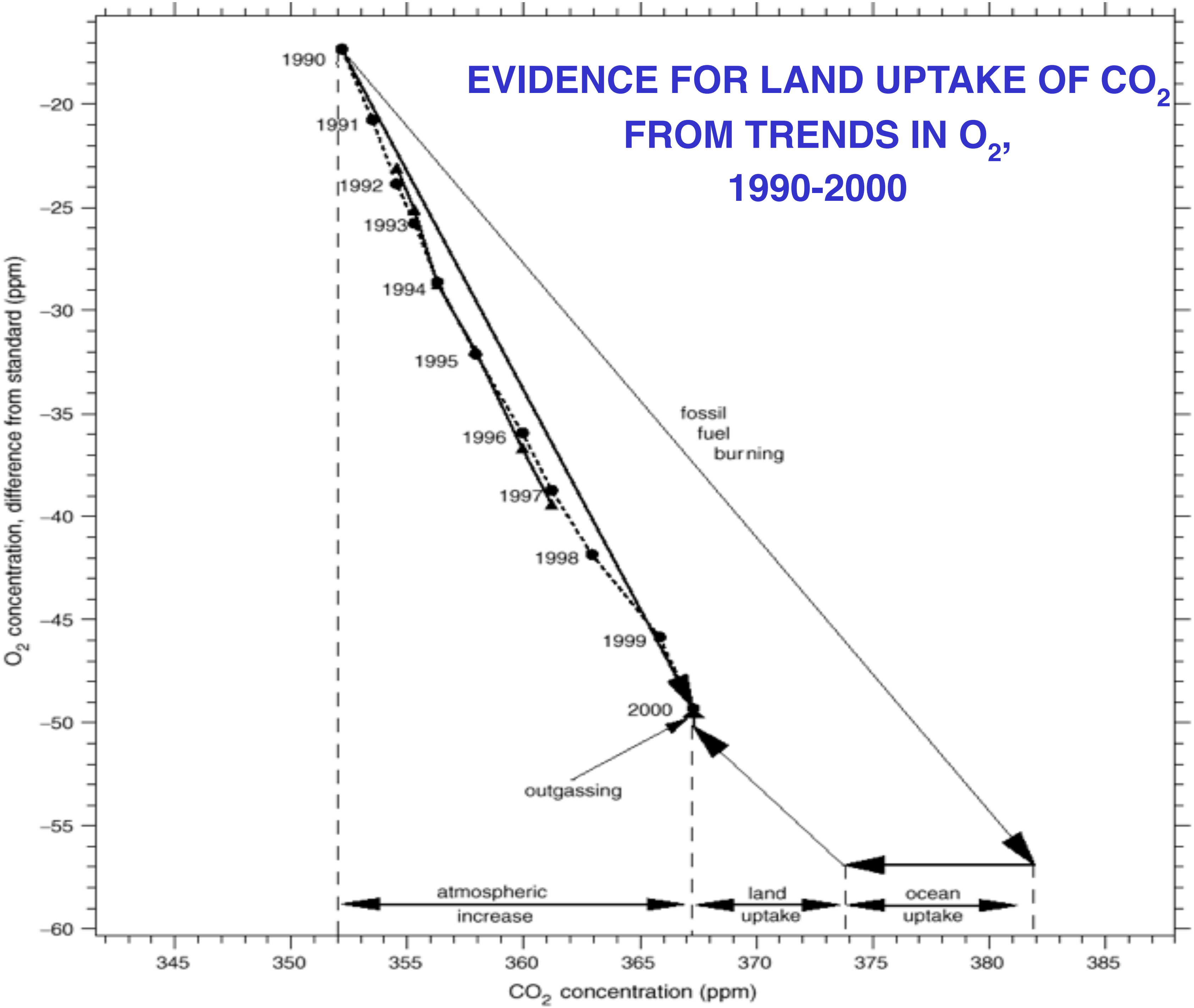


Decrease in O_2 as constraint on land uptake of CO_2

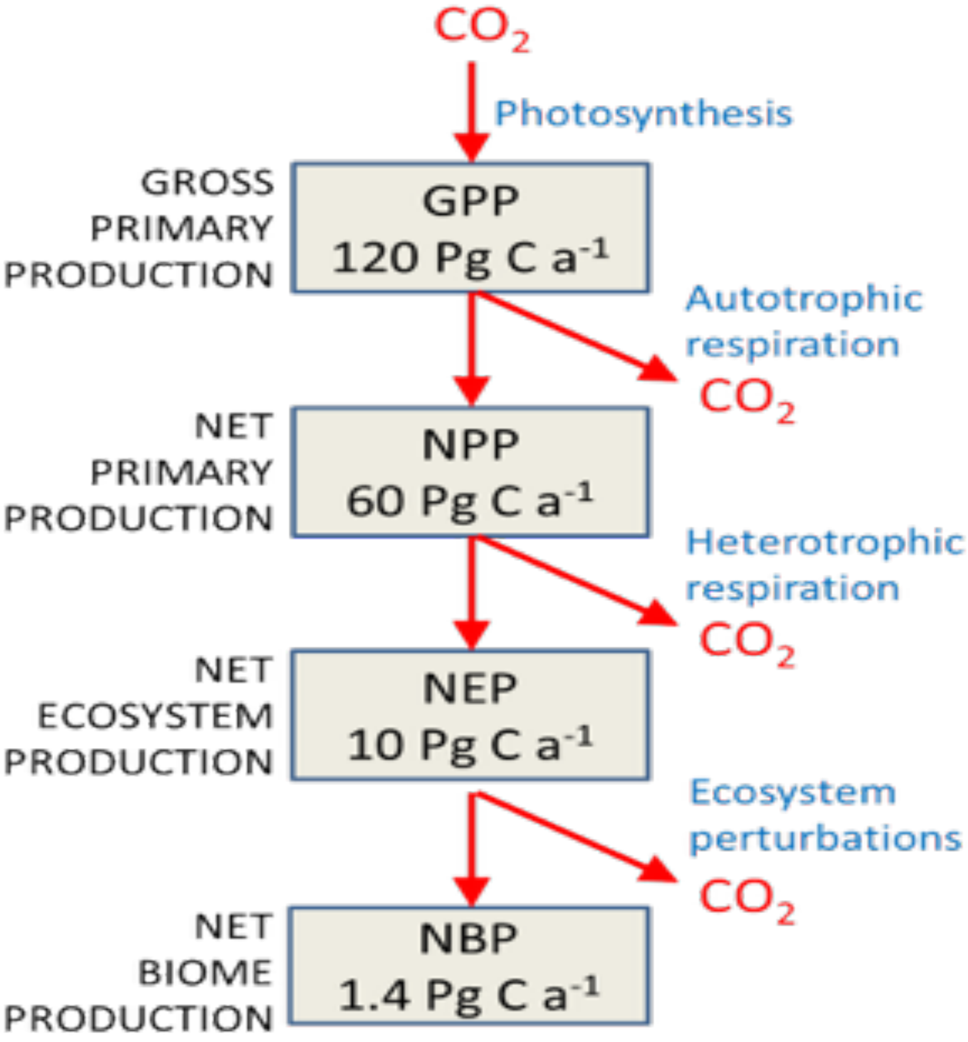


IPCC [2014]

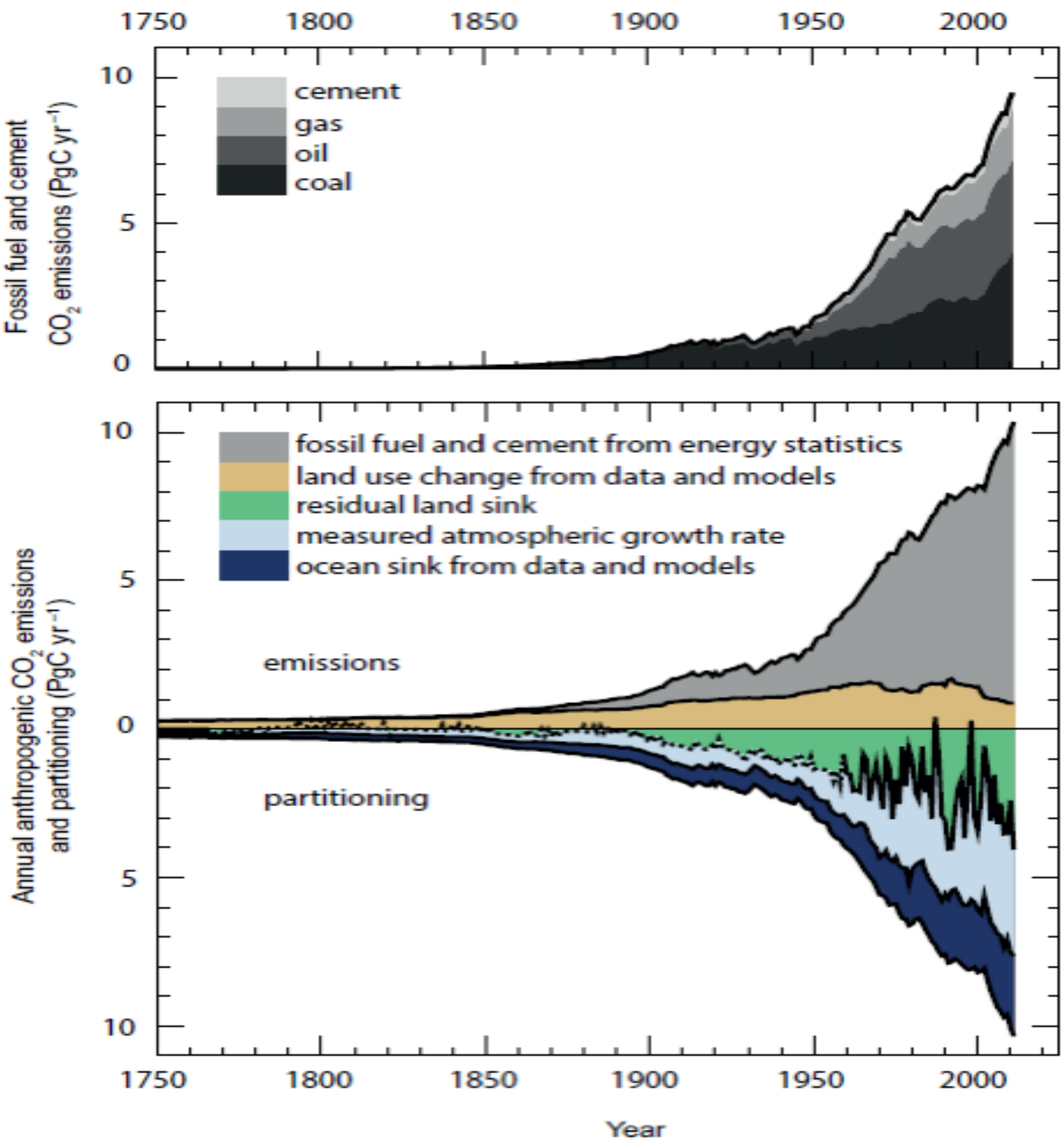
EVIDENCE FOR LAND UPTAKE OF CO_2 FROM TRENDS IN O_2, 1990-2000



Current net uptake of CO_2 by biosphere (1.4 Pg C yr^{-1}) is small residual of large atmosphere-biosphere exchange



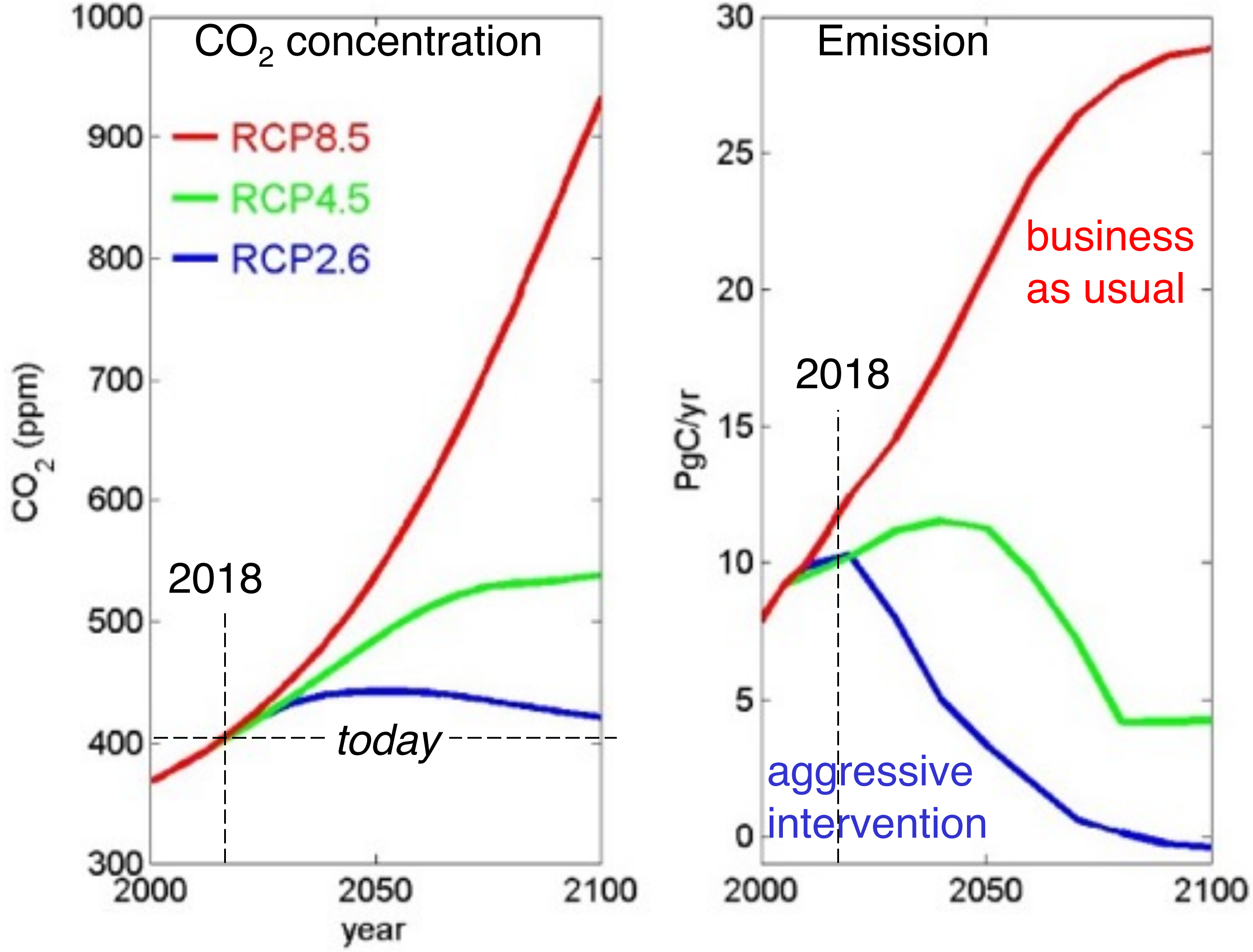
Carbon budget, 1750 present



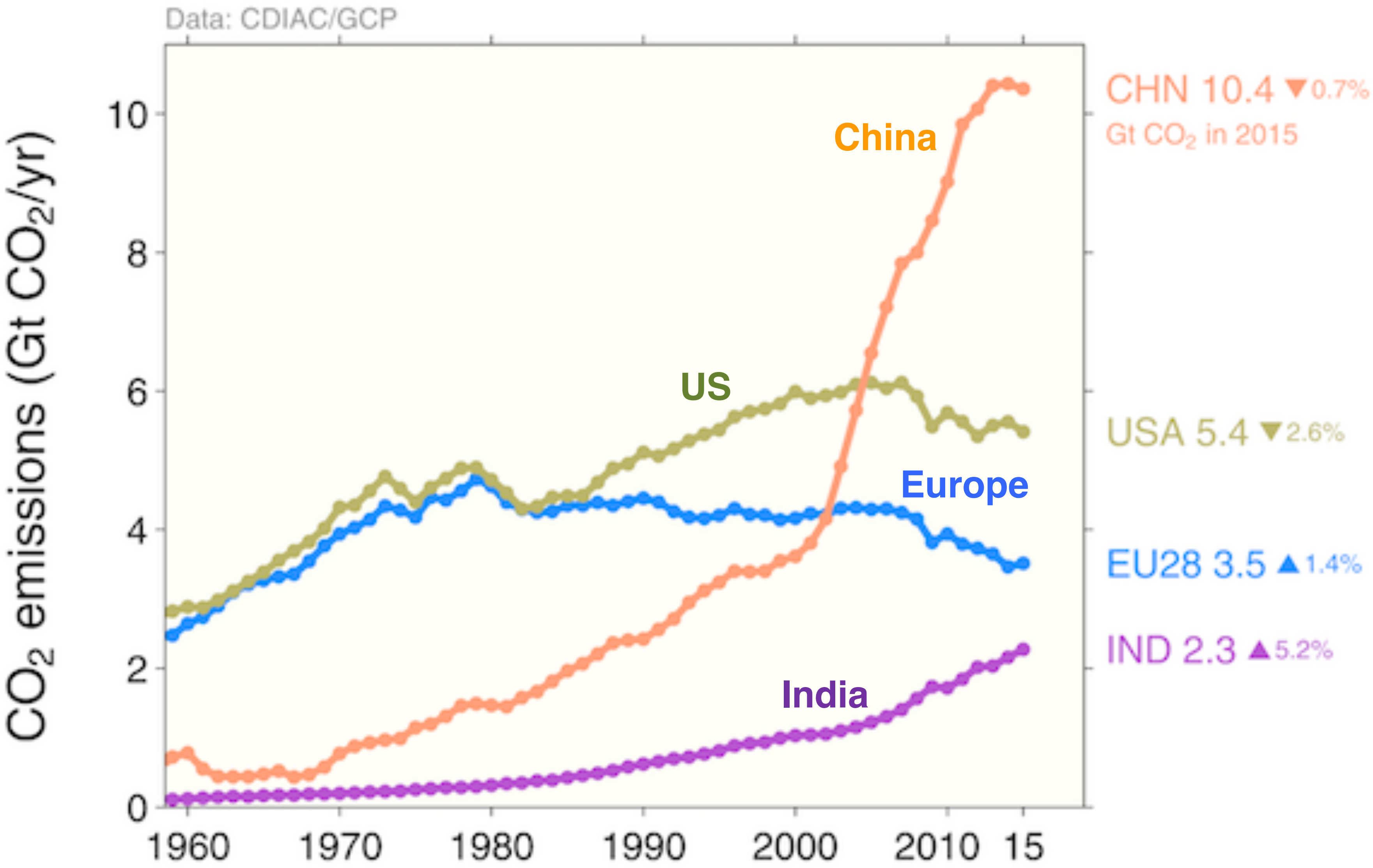
IPCC, 2014

Future projections of CO_2 emissions

IPCC Representative Concentration Pathways (RCP)



There is hope: CO$_2$ emissions are flattening out globally, decreasing in developed countries



Questions

1. From the standpoint of controlling atmospheric CO_2, is it better to heat your home with a wood stove or by natural gas?

2. You wish to fly from Boston to California on a commercial flight that consumes 100,000 lbs of jet fuel for the trip. The company offers - as an extra charge on your ticket - to make your personal trip carbon-neutral by planting trees. Does this seem practical, in terms of the number of trees that would need to be planted? And is this a reasonable long-term proposition for mitigating your personal "carbon footprint"?