LECTURE 5

Biogeochemistry of Global Carbon Cycle:

An Earth-System Perspective

Lecturer:

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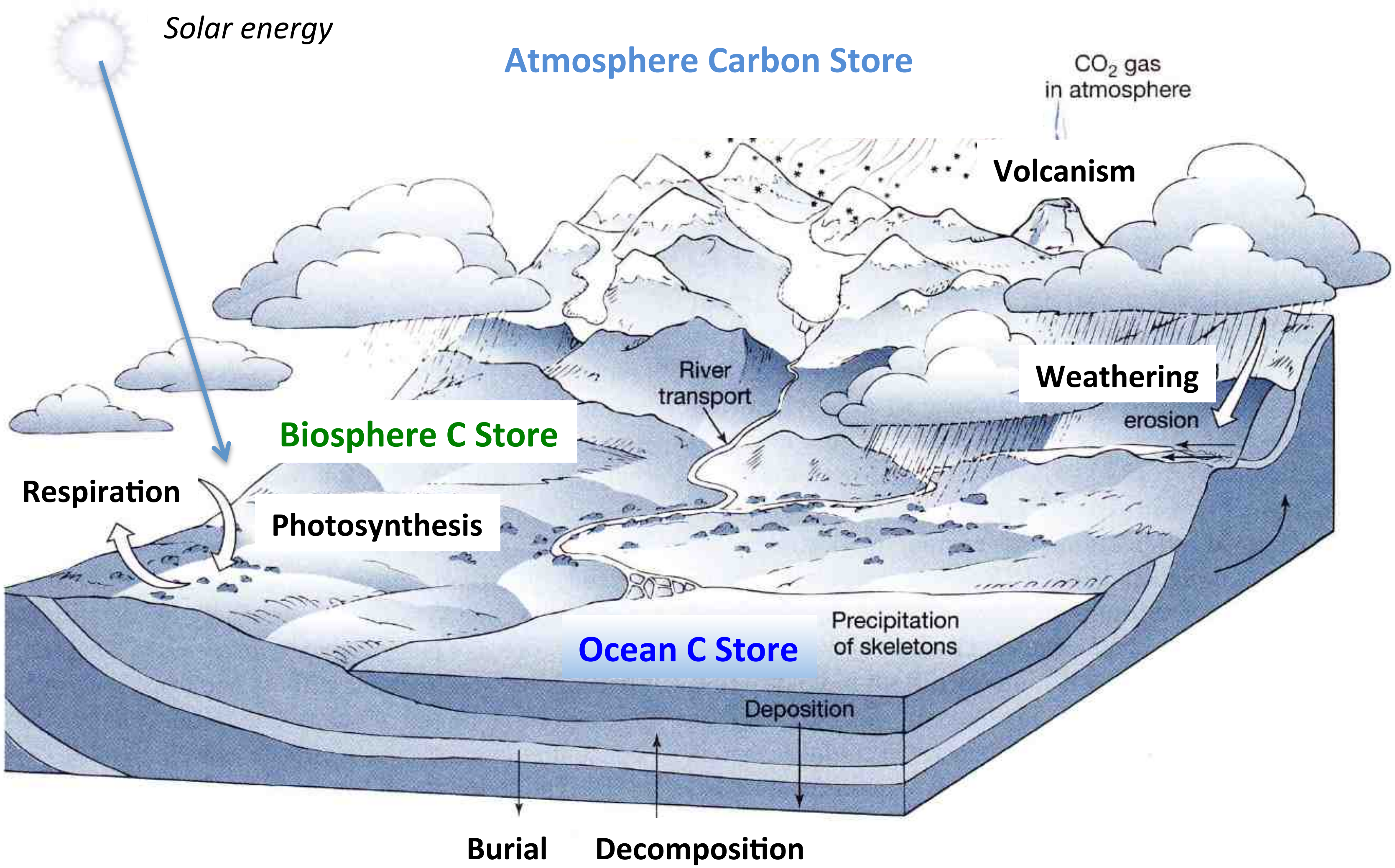
Arba Minch, Ethiopia, Oct 17, 2014

Lecture Outline

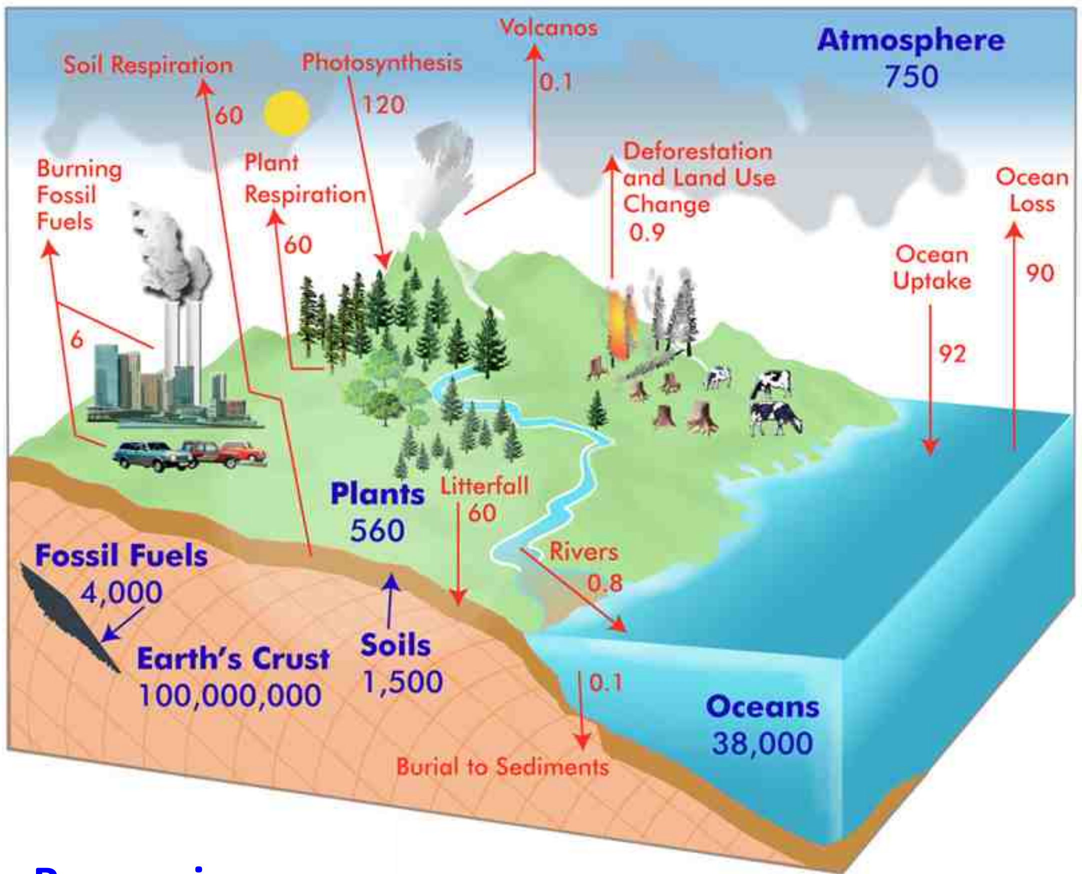
The main questions:

- Which inorganic and biological processes are important to the global C cycle
- What determines how carbon reservoirs (atm. CO_2) respond to cycle imbalances
- What is the fate of carbon released to atmosphere from burning of fossil fuels ?
- What feedback mechanisms on land and in the oceans regulate atm. CO_2 levels
- Oceanic alkalinity budget, and the air-sea CO_2 transfer and uptake rates

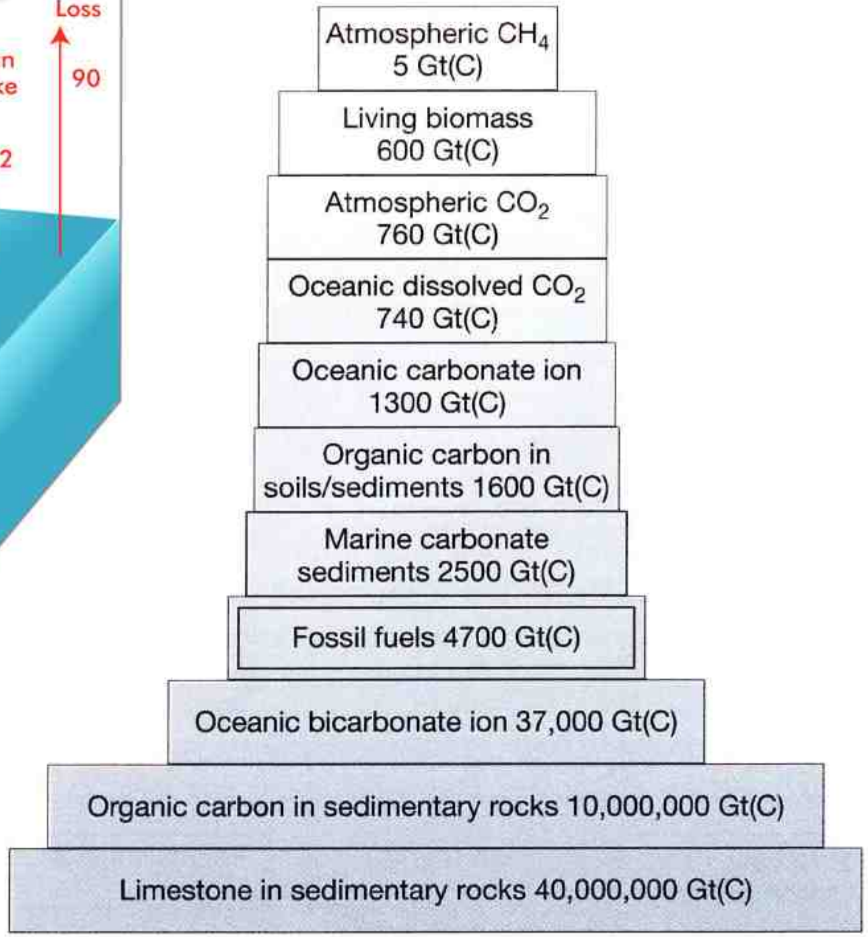
Components of the Global Carbon Cycle



Reservoirs and Fluxes in the Global Carbon Cycle



Reservoirs of carbon at or near Earth's Surface

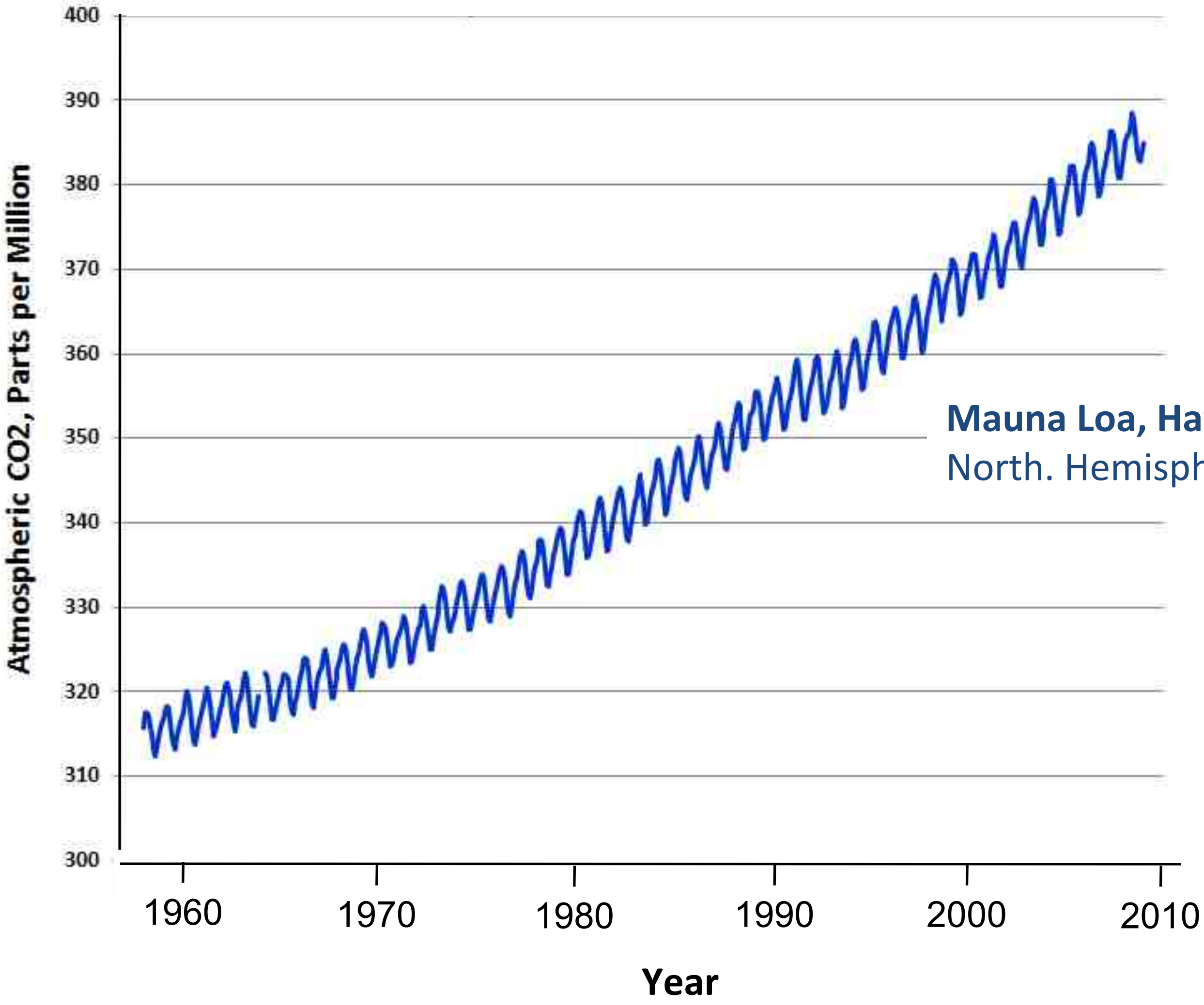


Reservoirs:
in Gigatons (Gt = 10^9 Tons) of carbon

Fluxes:
in Gigatons of carbon per year (Gt/yr)

The Global Carbon Cycle

The Keeling Curve: Atmospheric CO_2 concentrations measured at Mauna Loa



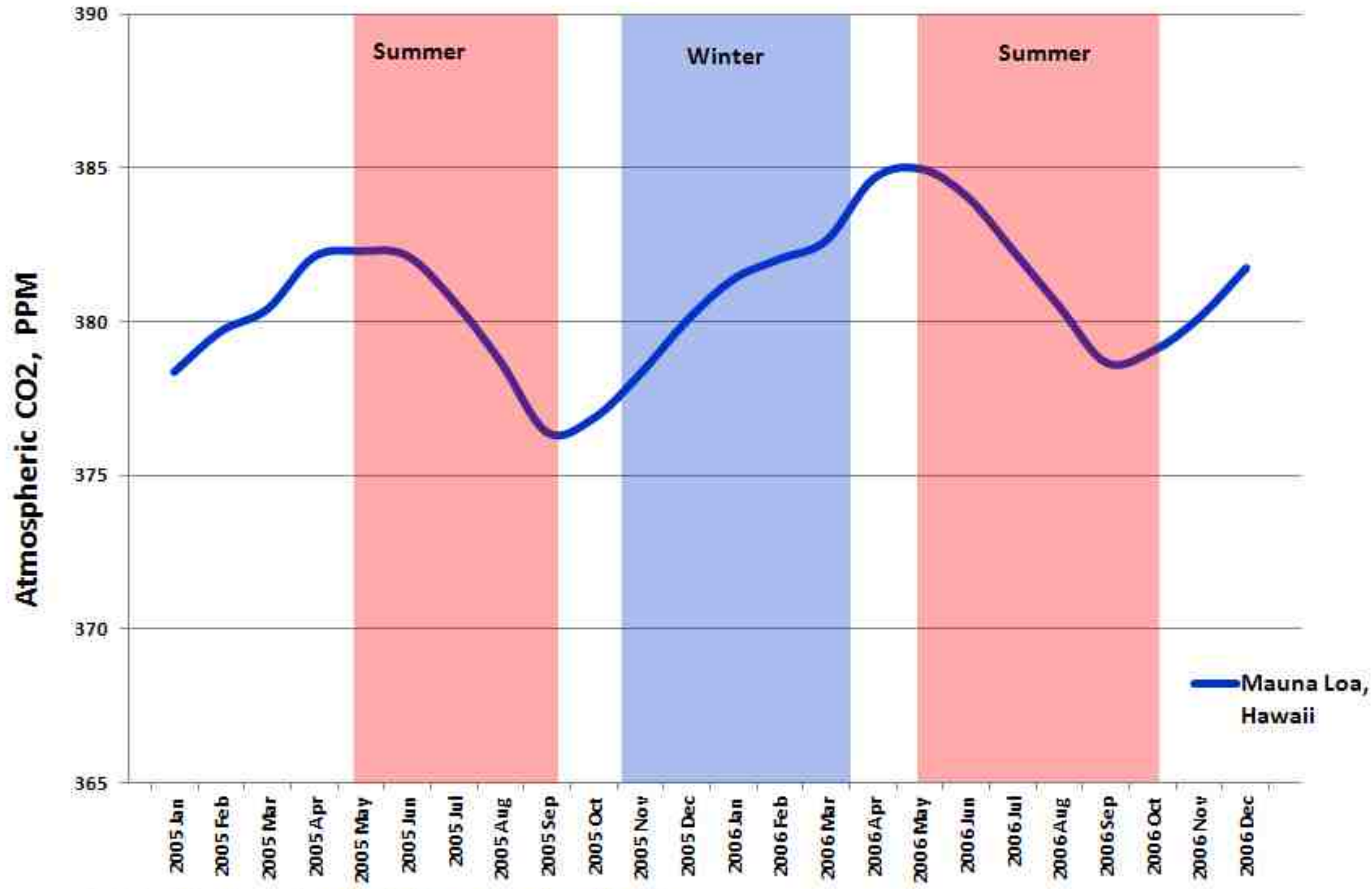
400.8 ppm CO_2
measured in 2014
(Mauna Loa)

280 ppm CO_2
pre-industrial

http://cdiac.ornl.gov

The Global Carbon Cycle

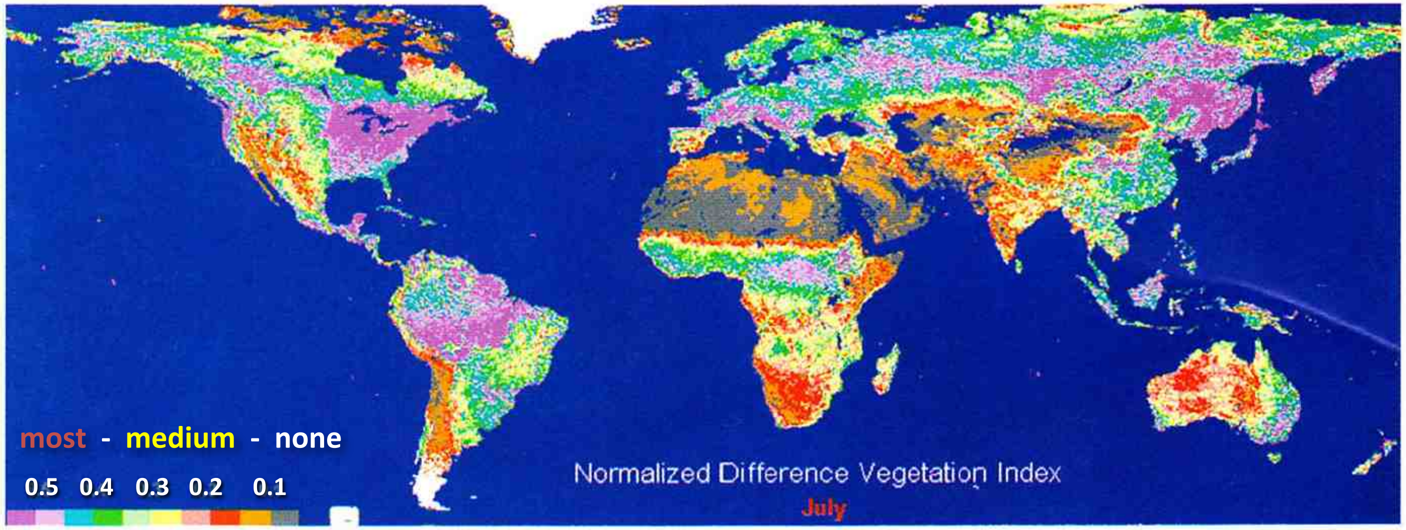
The Keeling Curve: Seasonal Cycle, 2005-2006, North. Hem. (17°N)



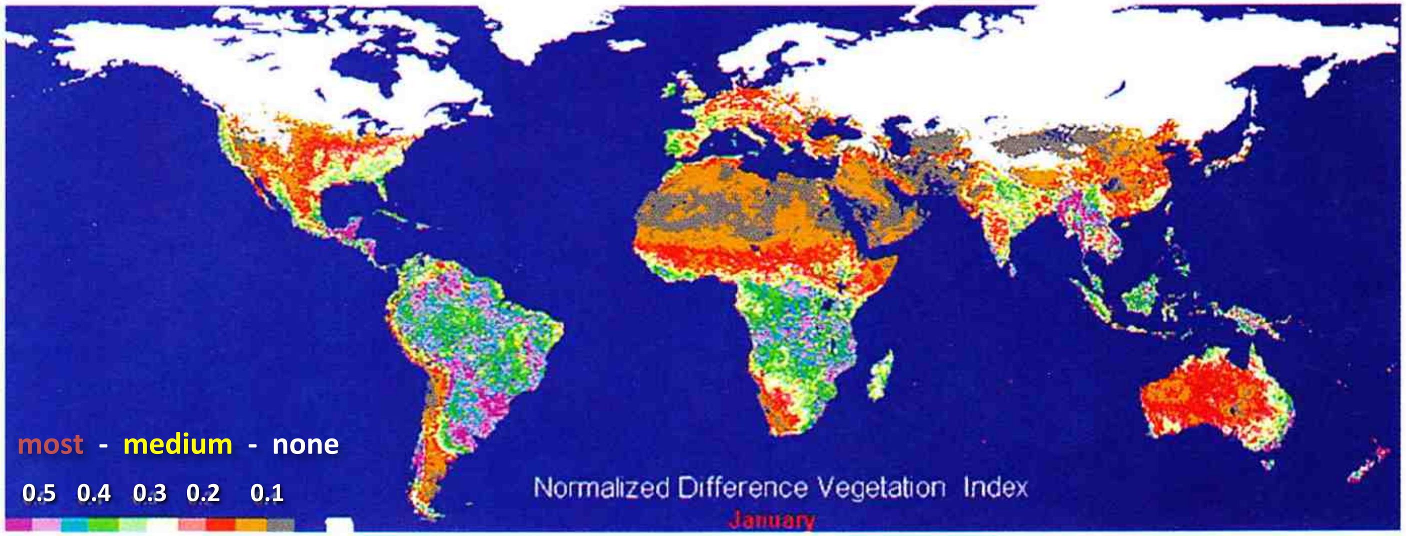
The Global Carbon Cycle

Satellite image of the global vegetation coverage (NOAA, NESDIS, ORA)

Summer

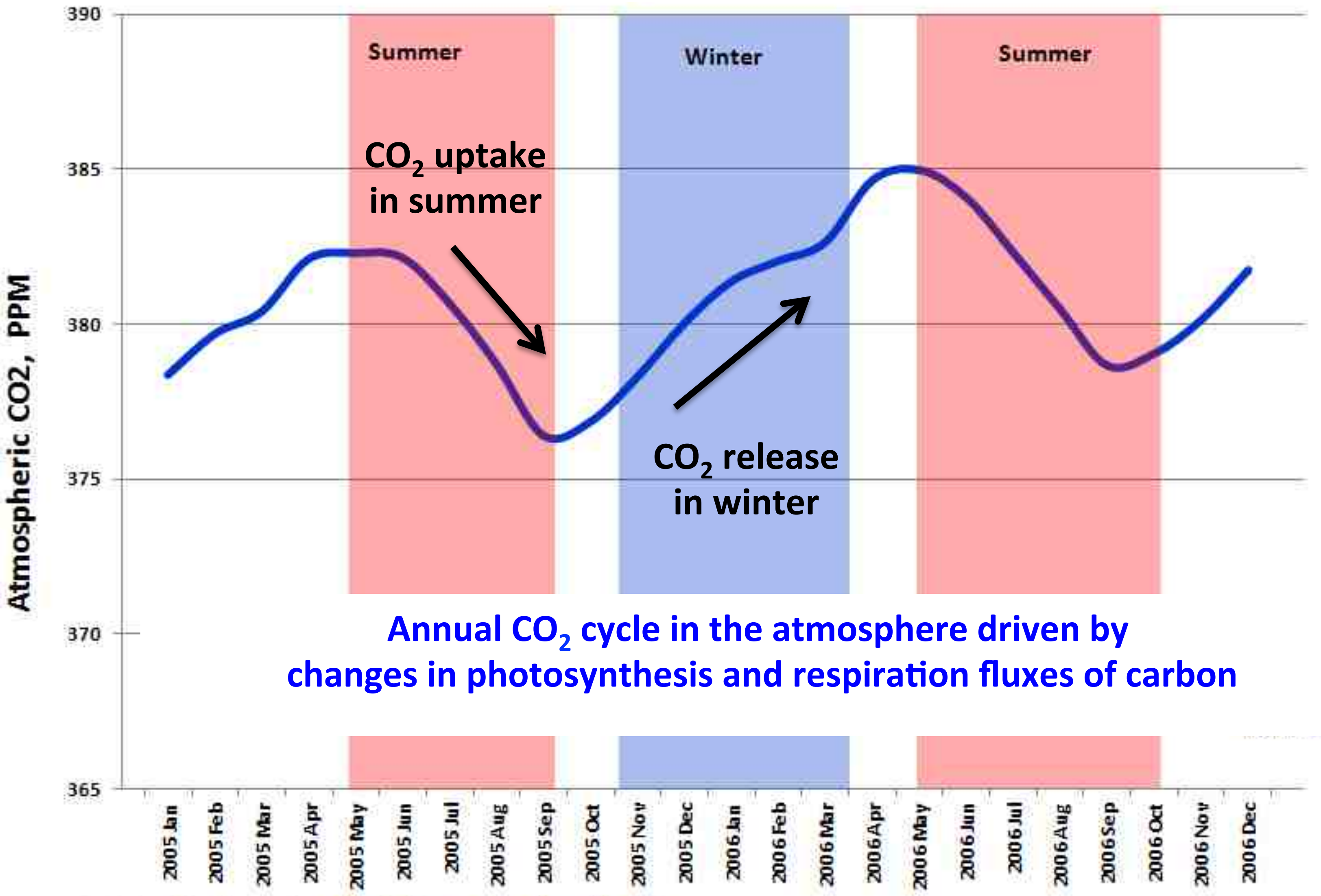


Winter



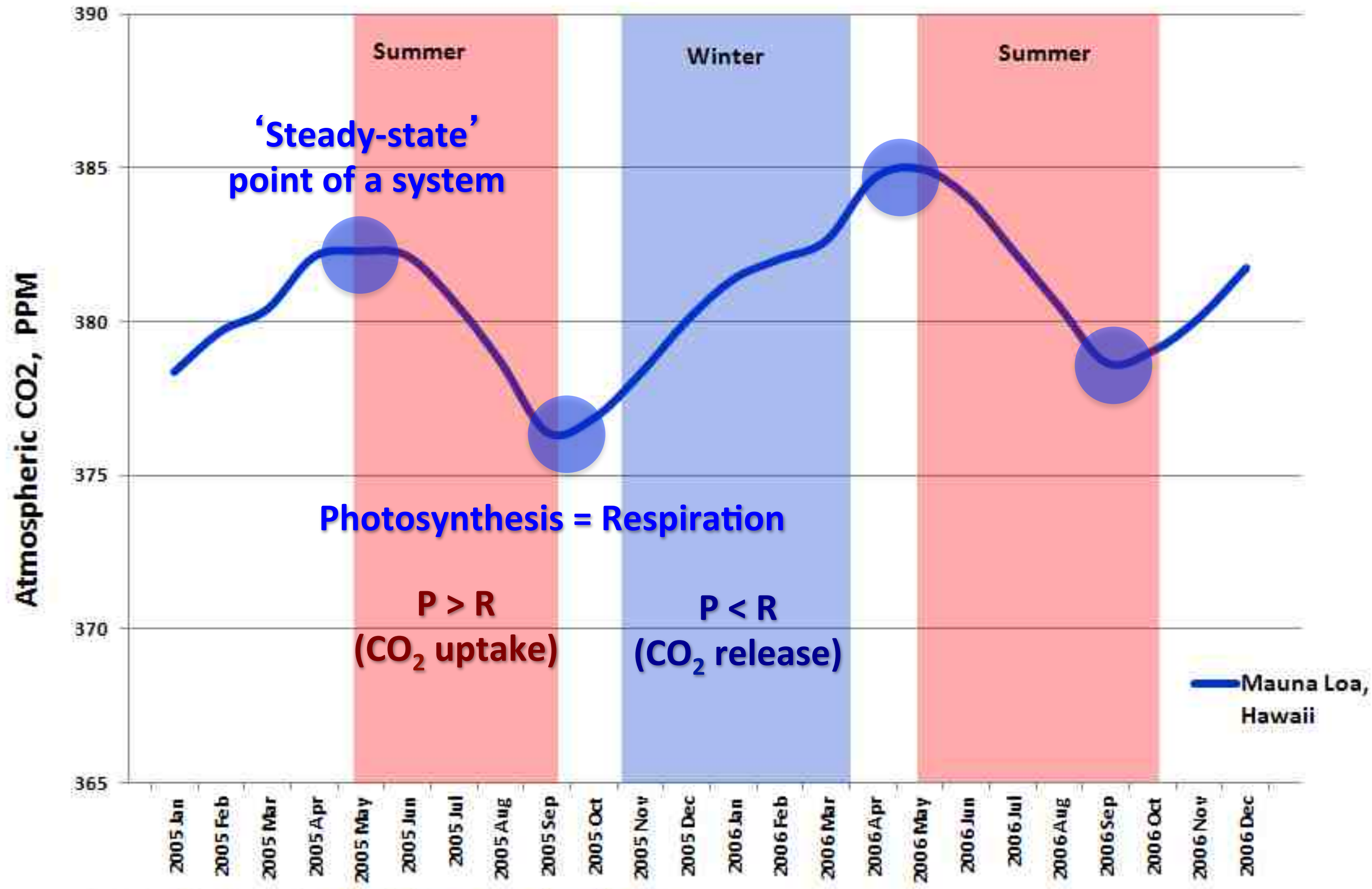
The Global Carbon Cycle

The Keeling Curve: Seasonal Cycle, 2005-2006, North. Hemisphere



The Global Carbon Cycle

The Keeling Curve: Seasonal Cycle, 2005-2006, North. Hemisphere



The Global Carbon Cycle

From the Earth's System point of view, the atmosphere is a *reservoir* of carbon

Atmospheric CO_2

760 Gton (C)

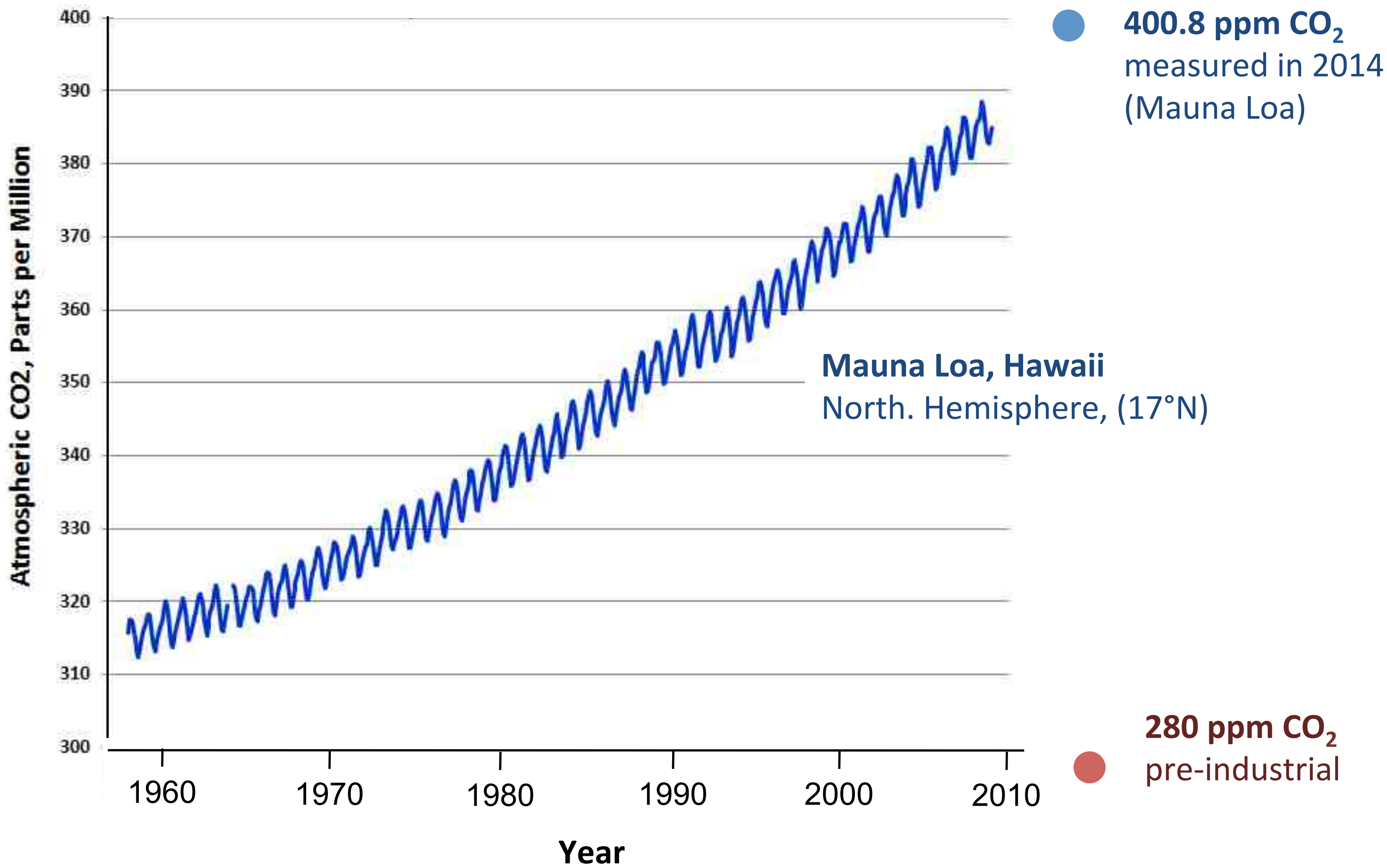
and the size of this reservoir (atmospheric CO_2 levels) can change in time due to changes in the inflow and outflow fluxes of carbon

$$\textbf{Residence time} = \frac{\textbf{reservoir size at steady state}}{\textbf{inflow or outflow rate}} = \frac{760\ \mathrm{Gt(C)}}{60\ \mathrm{Gt(C)/yr}} = 12.7\ \mathrm{yr}$$

Thus, on average, the CO_2 molecule spends in the Earth's atmosphere about 13 years

Anthropogenic Increase in Atmospheric CO_2

The Keeling Curve: Atmospheric CO_2 concentrations measured at Mauna Loa

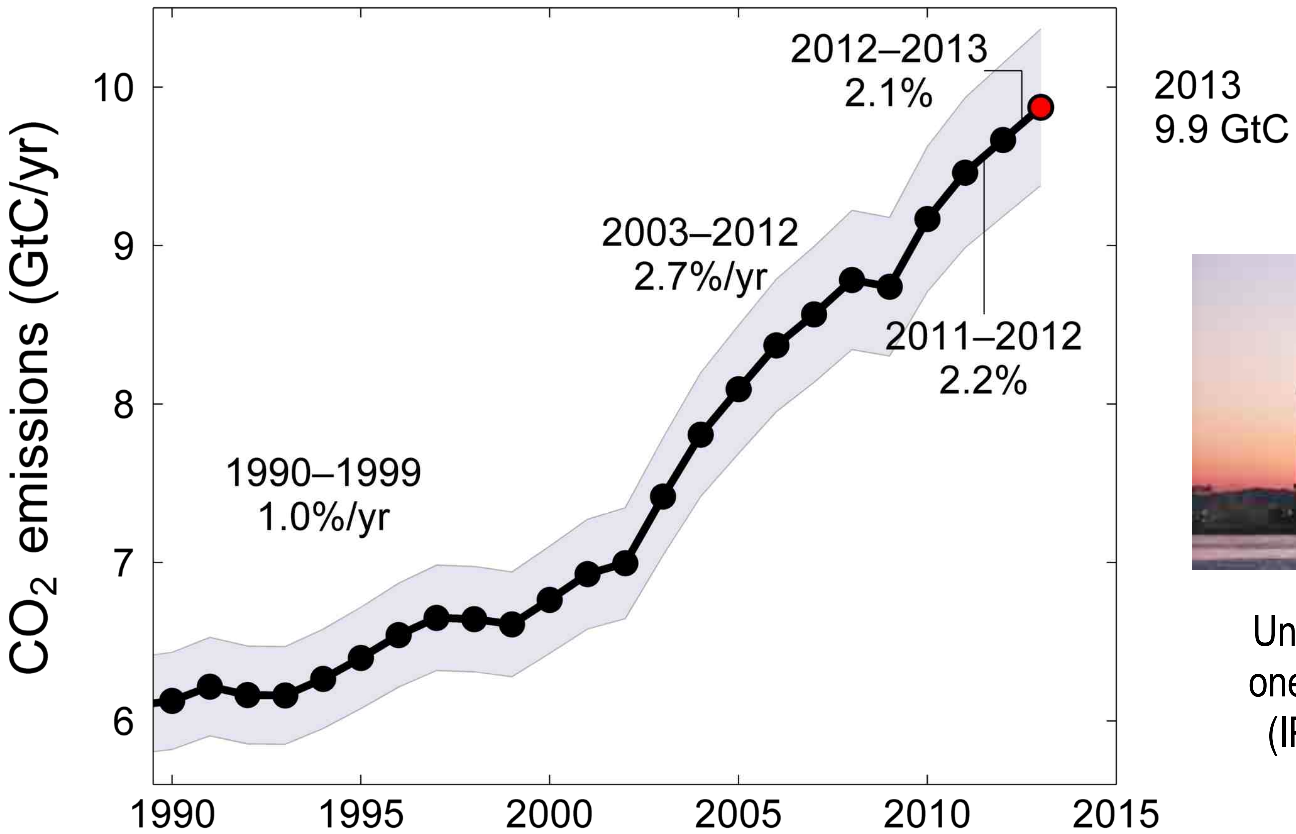


http://cdiac.ornl.gov

Anthropogenic CO_2 Emissions

Global fossil fuel and cement emissions: 9.7 ± 0.5 GtC in 2012

(about 50% increase compared to 1990)



Uncertainty is ±5% for one standard deviation (IPCC “likely” range)

Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic CO_2 Emissions

All the data is shown in GtC

1 Gigatonne (Gt) = 1 billion tonnes = 1×10^{15}g = 1 Petagram (Pg)

1 kg carbon (C) = 3.664 kg carbon dioxide (CO_2)

1 GtC = 3.664 billion tonnes CO_2 = **3.664 Gt CO_2**

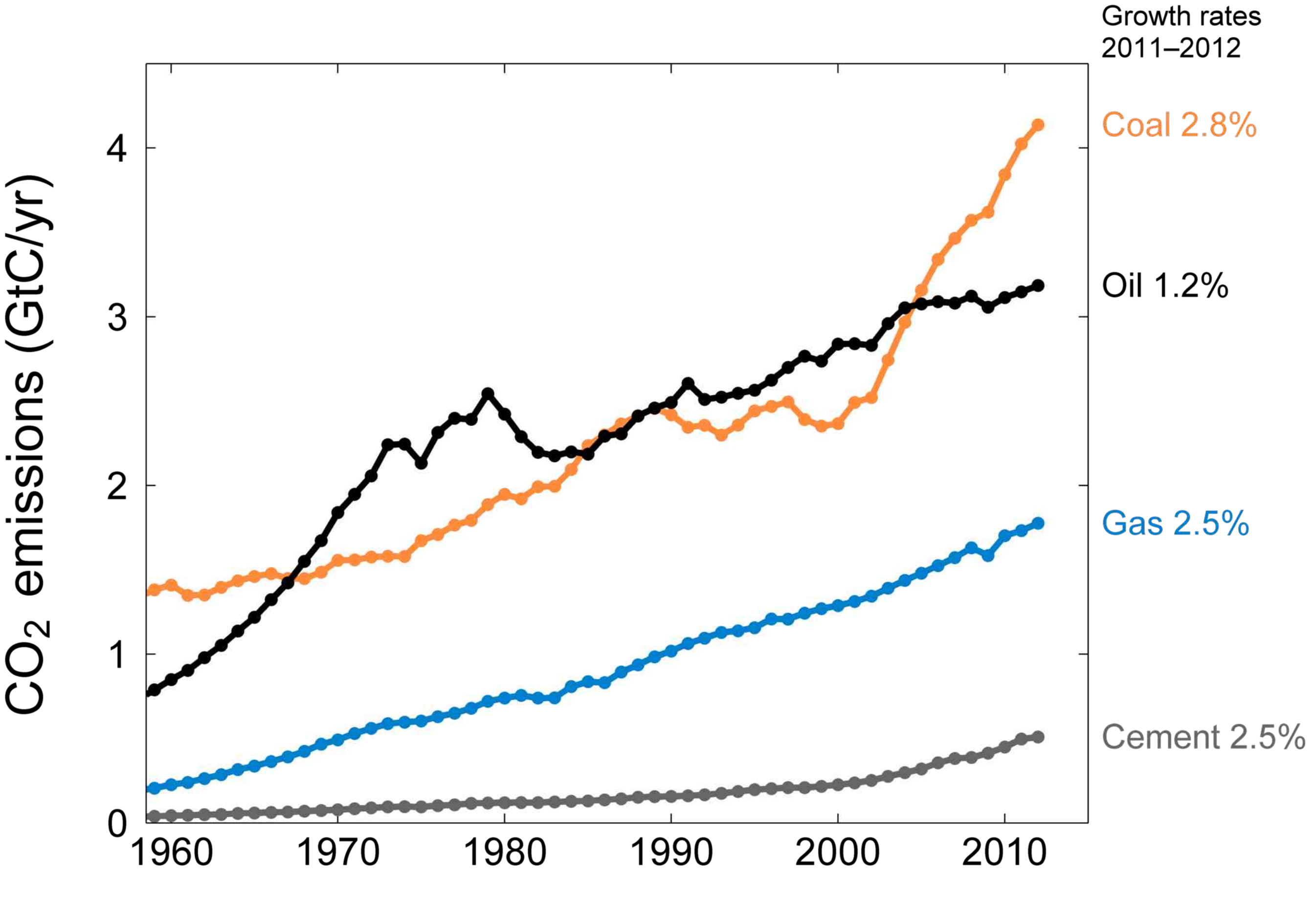
If you want to convert the carbon fluxes (GtC) to CO_2 fluxes ($GtCO_2$), you need to multiply the carbon fluxes by 3.664

Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic CO_2 Emissions

Share of Global Fossil Fuel Emissions in 2012:

Coal (43%), **Oil** (33%), **Gas** (18%), **Cement** (5%), **Flaring** (1%, not shown)



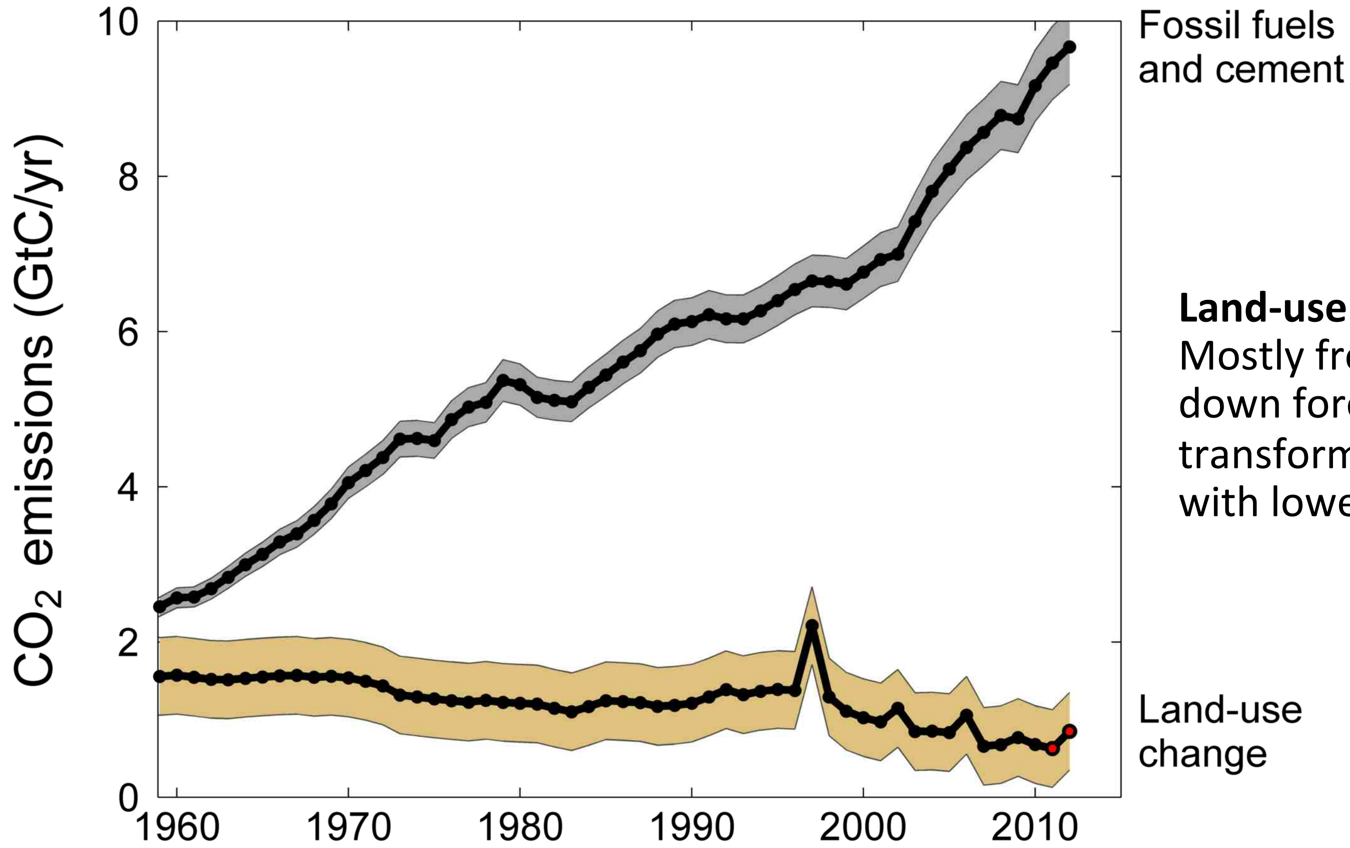
Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Gas flaring: the burning of natural gas associated with the oil extraction processes

Anthropogenic CO_2 Emissions

Total Global Emissions: 10.5 ± 0.7 GtC in 2012

Percentage land-use change: 38% in 1960, only 8% in 2012

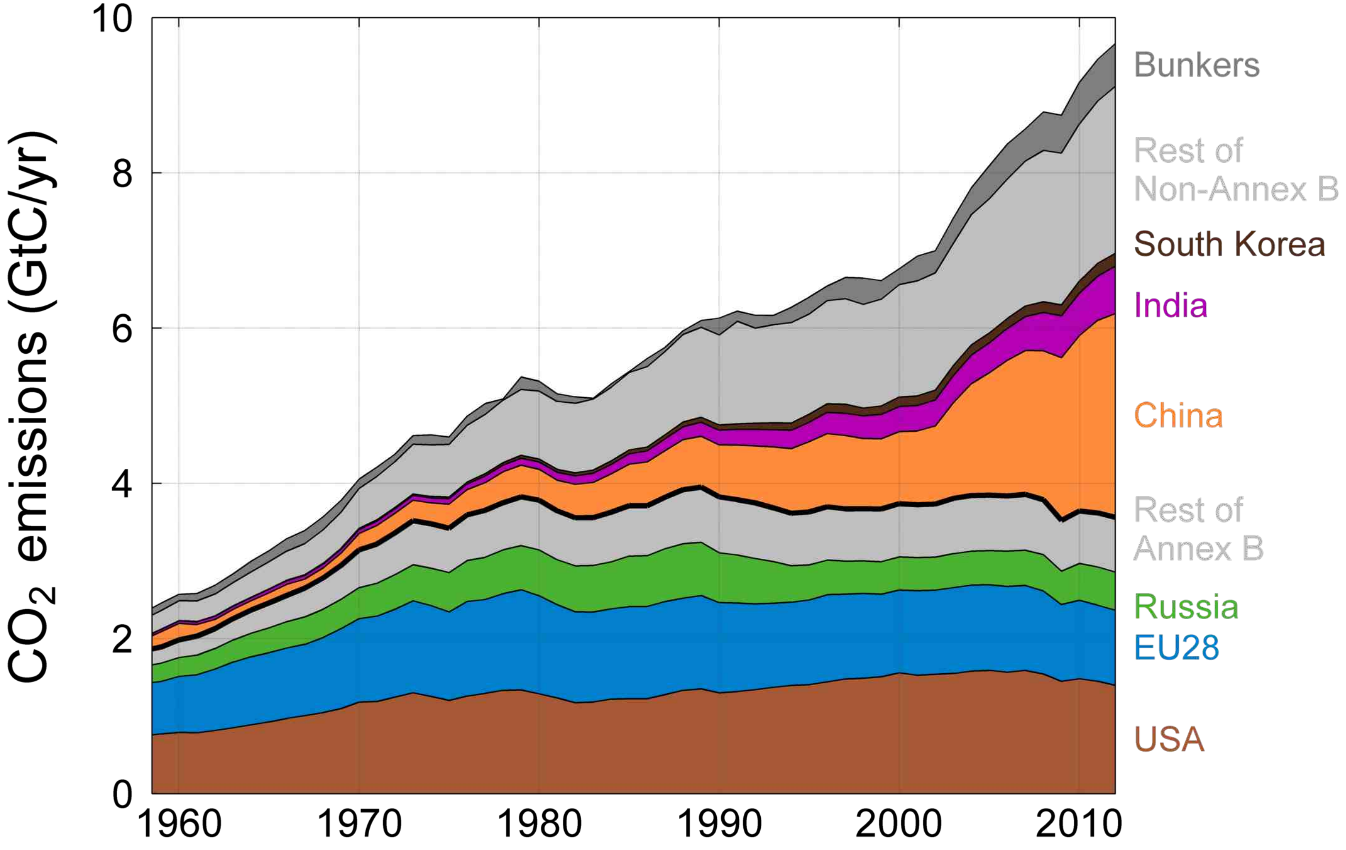


Land-use CO_2 Emissions:
Mostly from cutting down forests, and their transformation to grasslands with lower CO_2 storage

Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic CO_2 Emissions

Breakdown of Global Emissions by Country

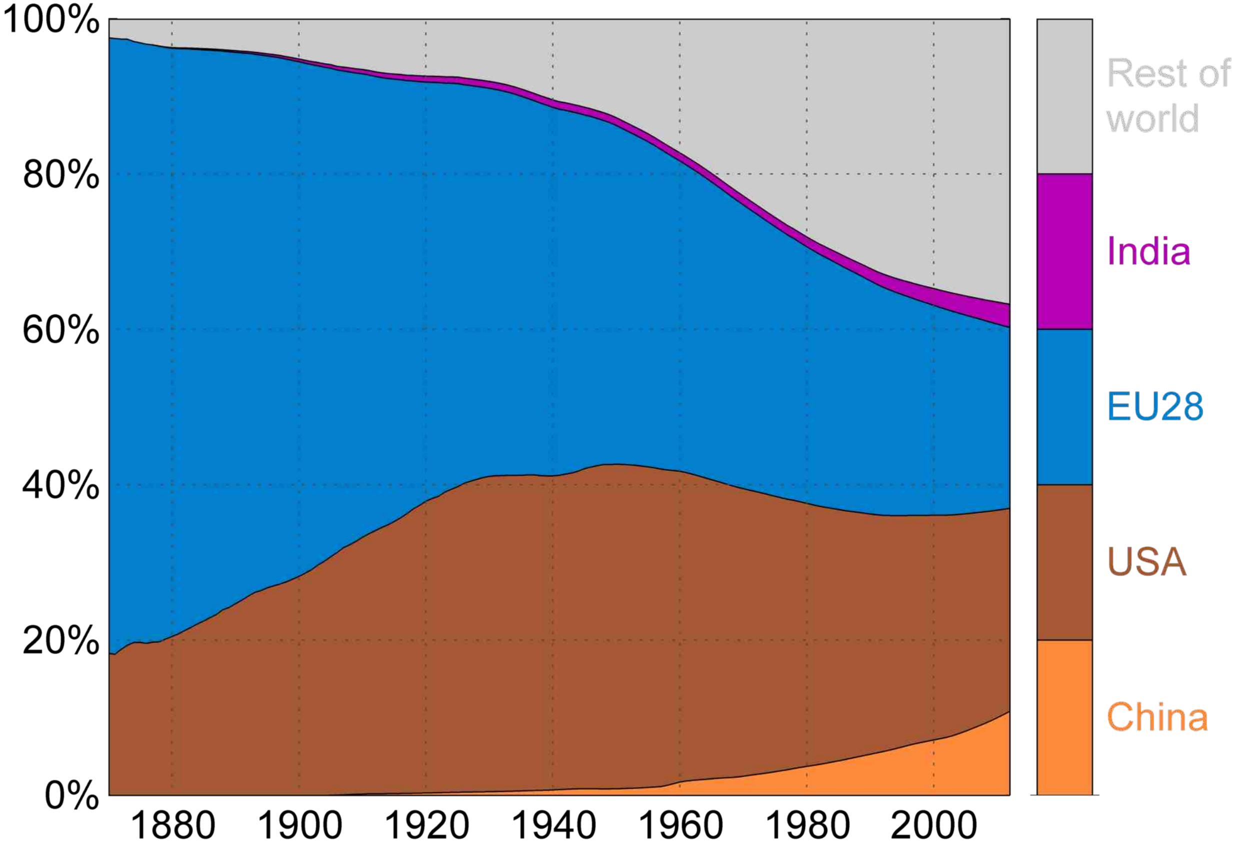


Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic CO_2 Emissions

Historical Cumulative Emissions by Country

USA (26%), EU28 (23%), China (11%), and India (4%) covering 64% of the total share

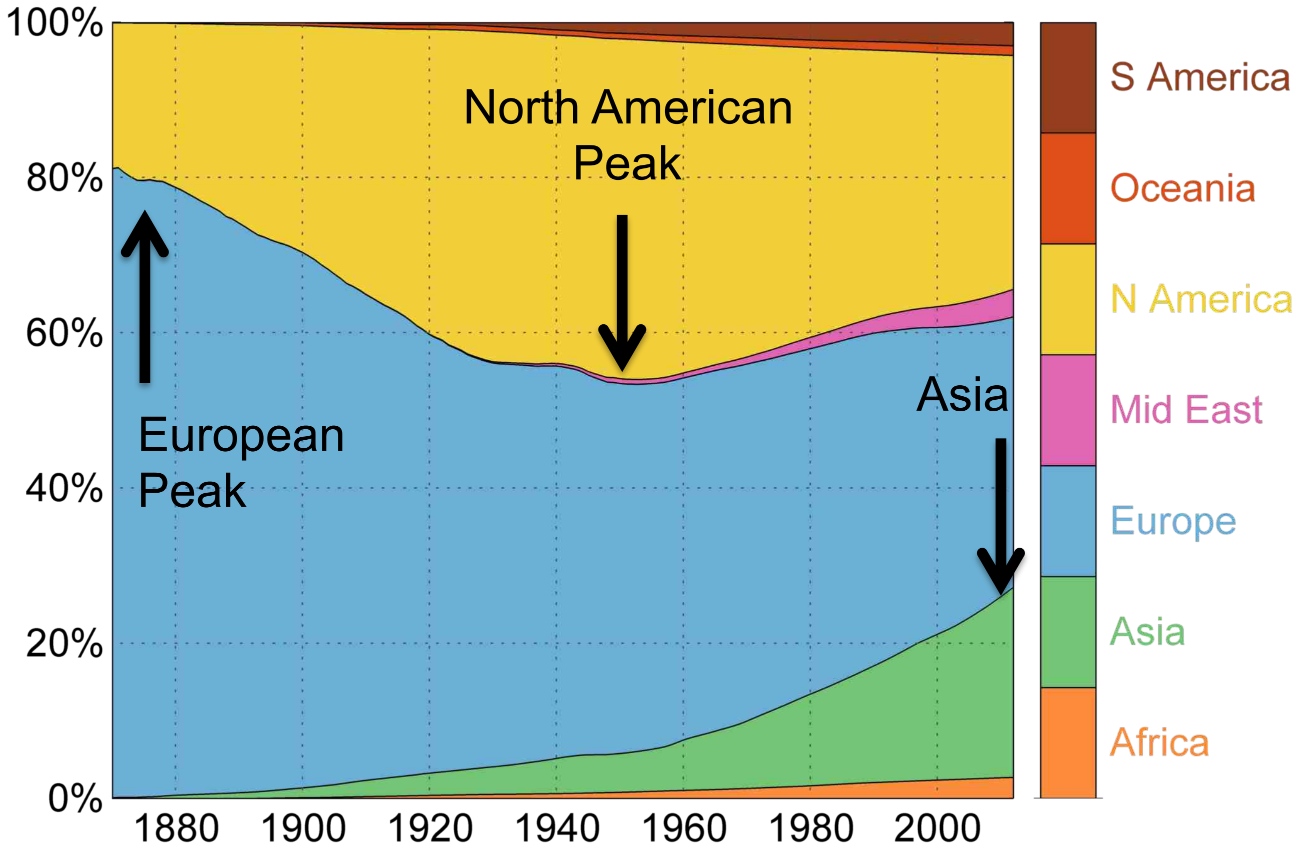


Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic CO_2 Emissions

Historical Cumulative Emissions by Region

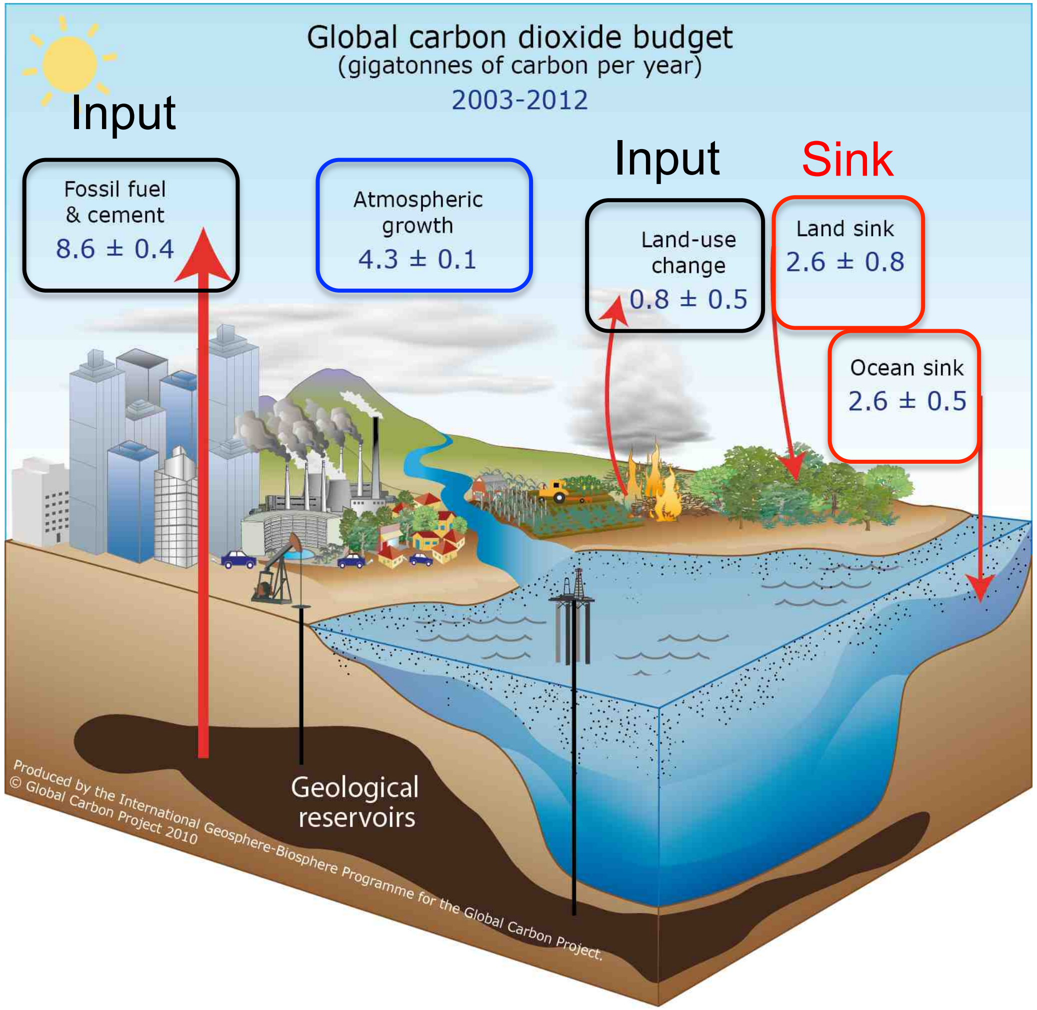
N. America and Europe responsible for most cumulative emissions, but Asia is growing fast …



Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Global Carbon Budget - Anthropogenic Fluxes

Major Input and Output Fluxes of Carbon due to Human Activities
Globally averaged fluxes for the period of one decade 2003 to 2012 (GtC/yr)



Only about 50% of the human produced CO_2 inputs stays in atmosphere

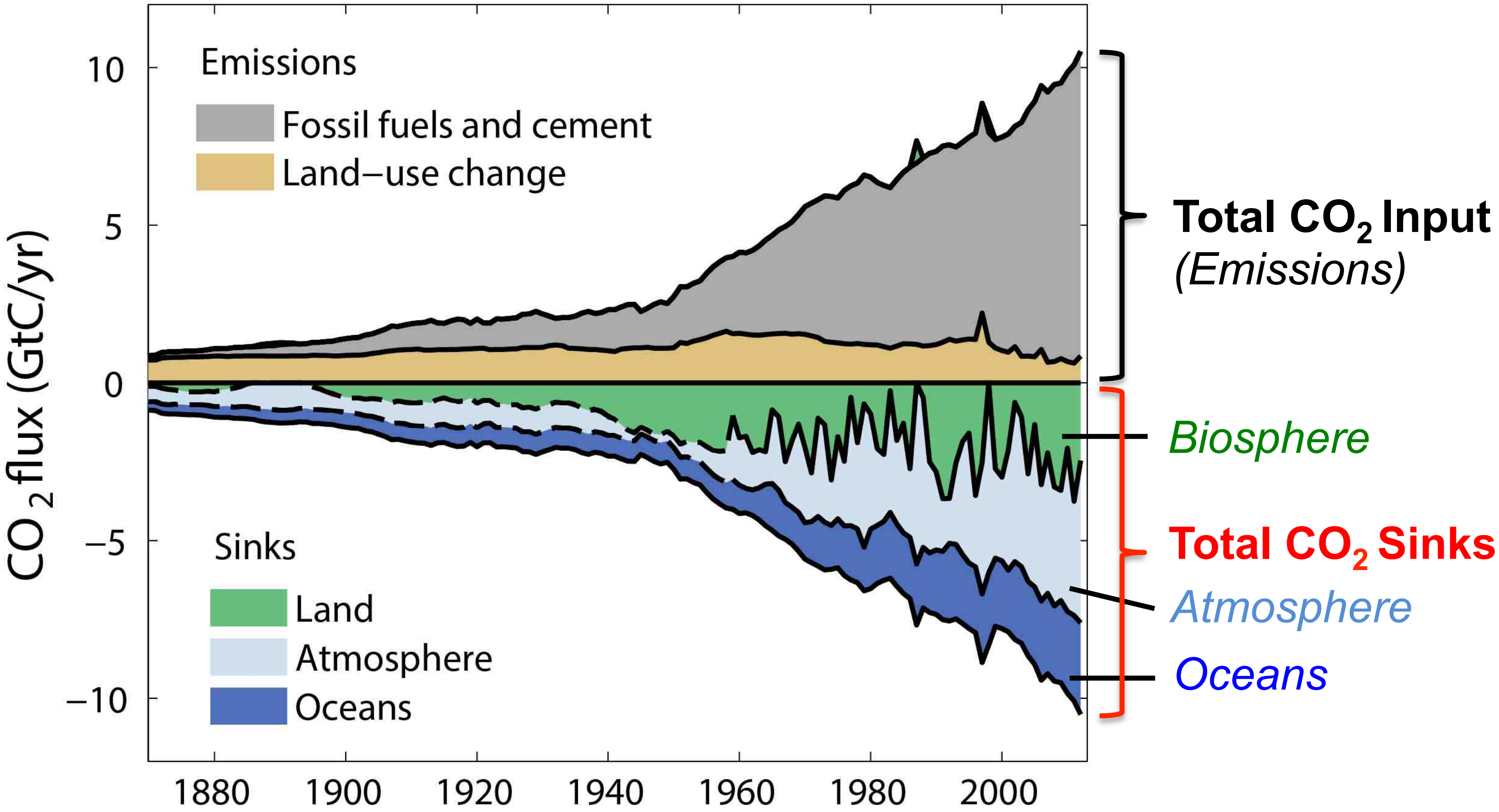
Remaining 50% is taken up by the oceans (25%) and by the terrestrial biosphere (also ca. 25%)

Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic Perturbation to Global Carbon Cycle

Global Balance of CO_2 Input and Output Fluxes over Time

Average sinks since 1959: 45-50% atmosphere, 25-28% land, 25-27% ocean

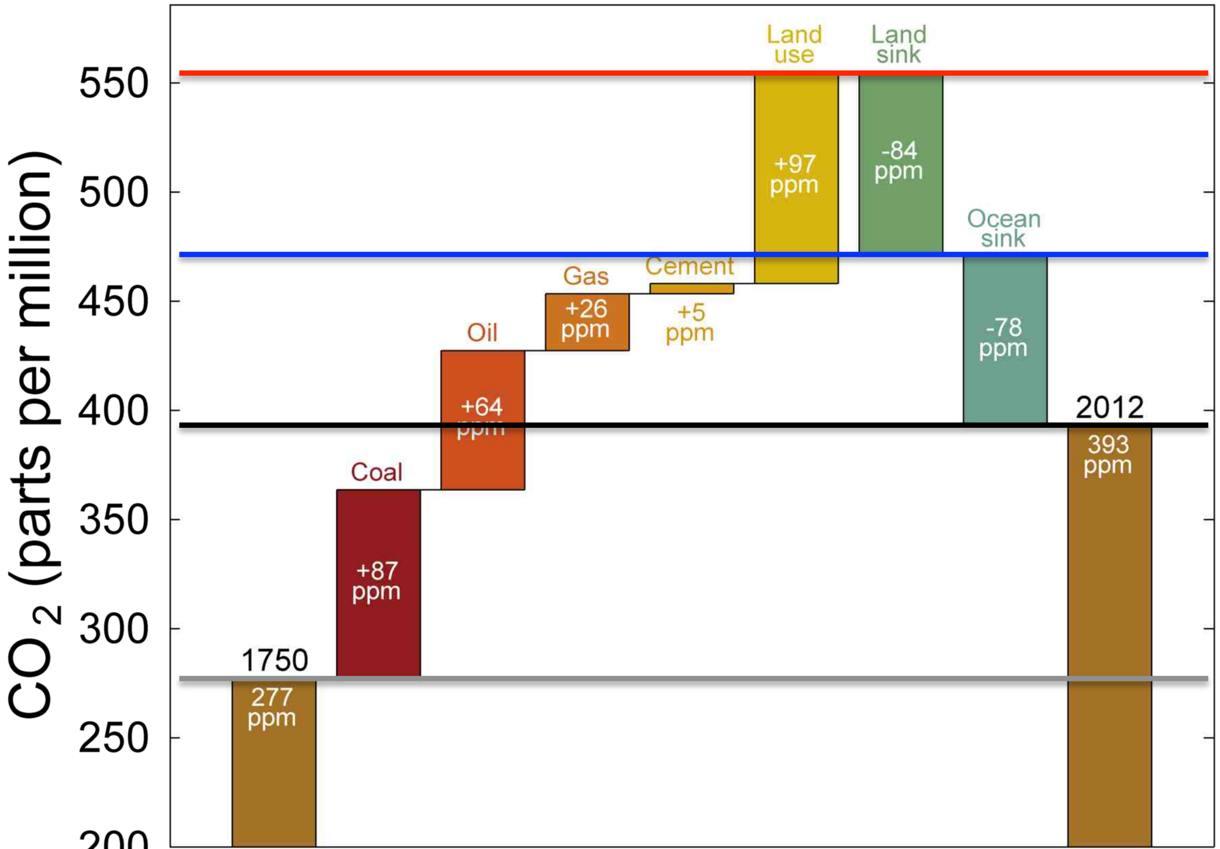


Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Anthropogenic Perturbation to Global Carbon Cycle

Cumulative Contributions to Global Carbon Budged from 1750

Contributions are shown in parts per million (ppm)



Today CO_2 levels without "land" and "ocean" sinks

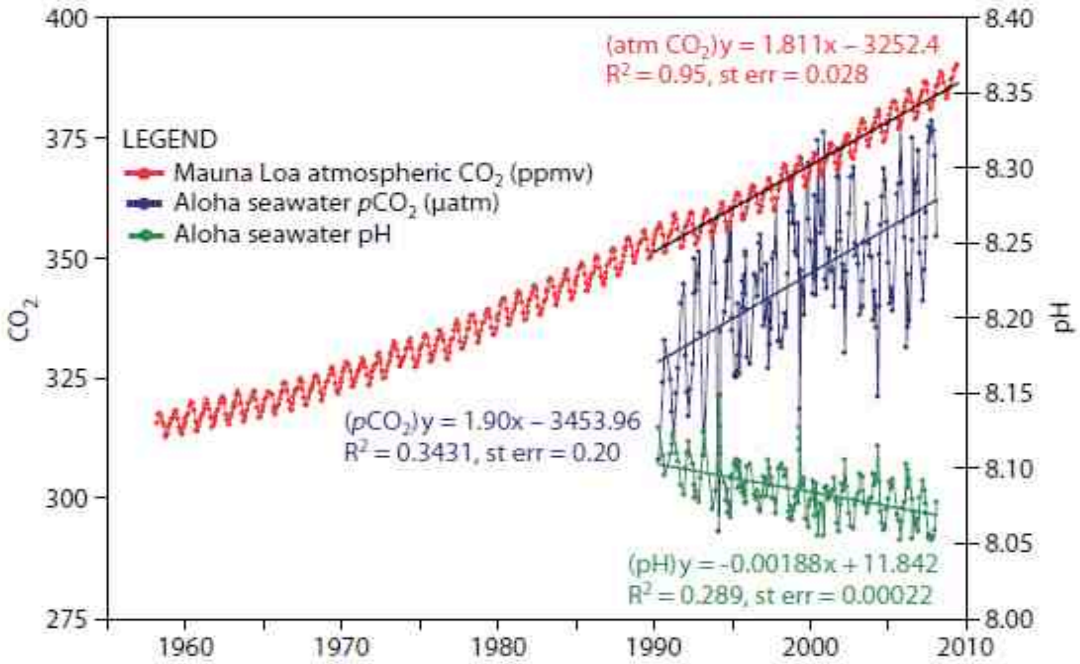
Today CO_2 levels without ocean sink

Today CO_2 levels

Preindustrial levels

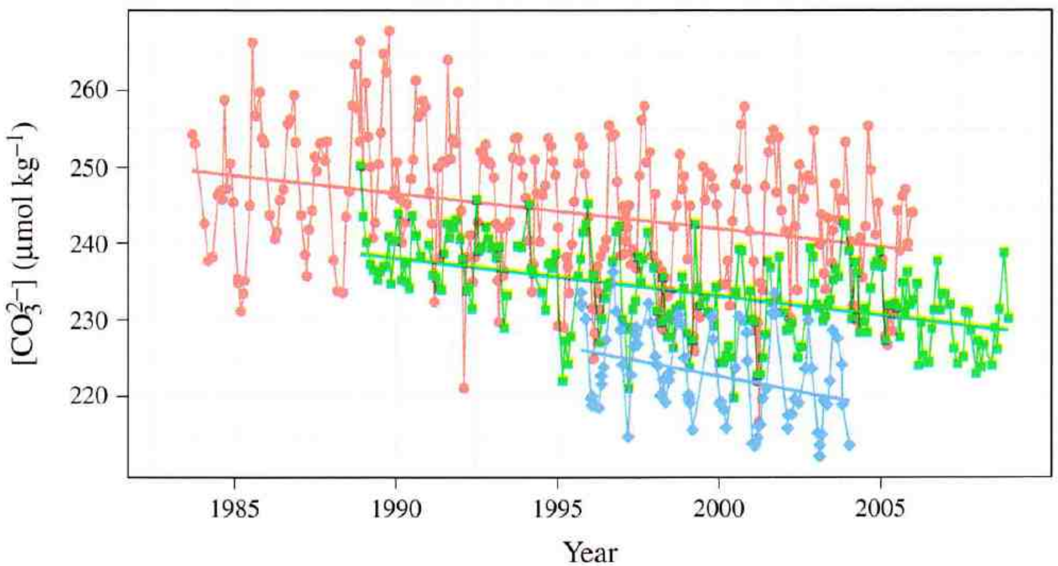
Source: Le Quéré et al 2013 (Global Carbon Project 2013)

Changes in Seawater pH and CO_3^{2-} Measured at Hawaii Site



ALOHA (green), BATS (red), and ESTOC (blue)

Studies showed that since the Industrial Revolution the global average pH of surface ocean water has decreased by ~ 0.11 unit



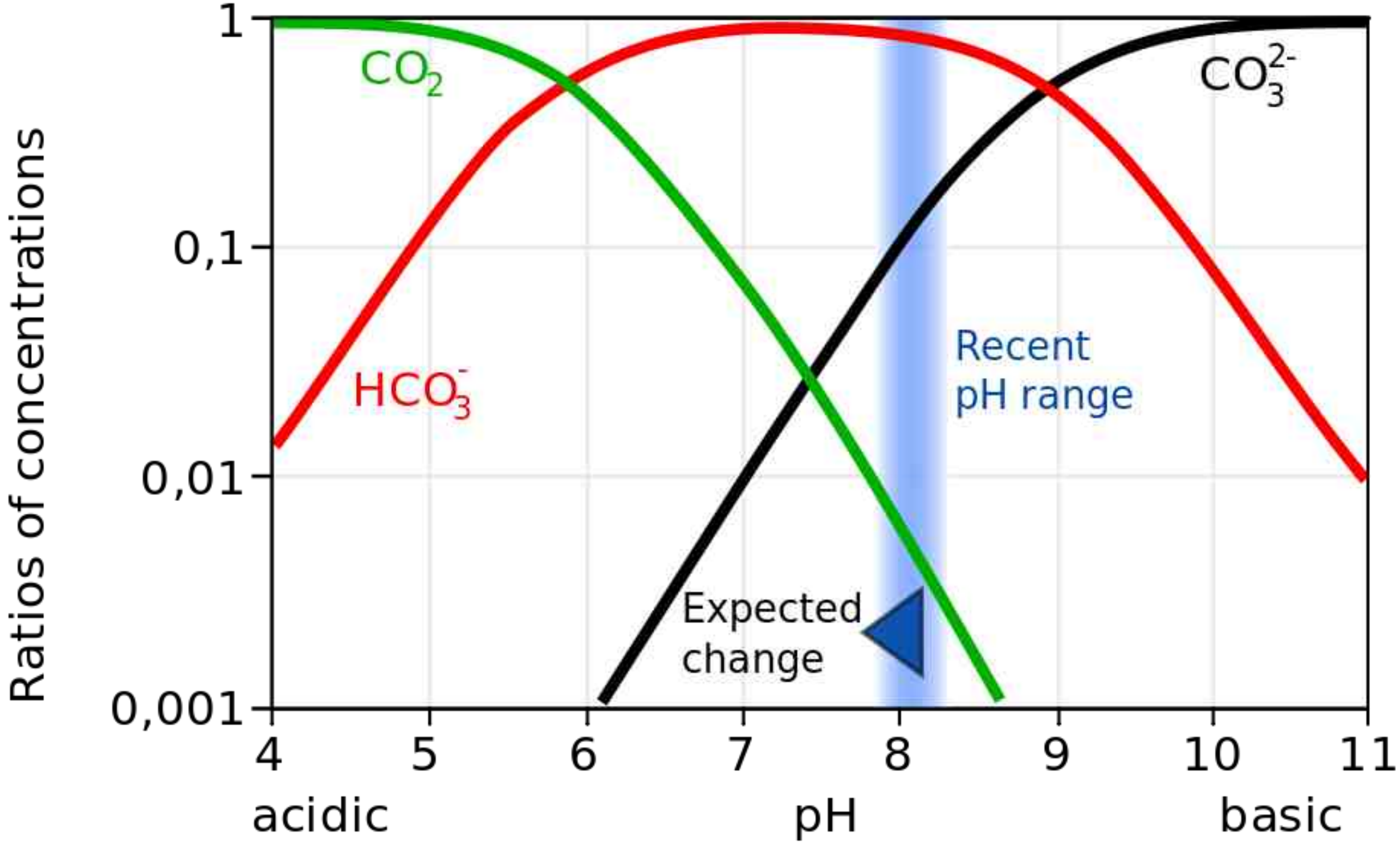
This 0.1 unit shift in the pH corresponds to a large increase, ~30%, in the hydrogen ions (H^+) concentration in the ocean, as pH scale is logarithmic!

From Mackenzie et al. 2011

Seawater Carbonate Chemistry – Ocean Acidification

CO_2 *(atm)* + H_2O *(ocean)* ⇔ H_2CO_3 ⇔ HCO_3^- + H^+ *(acidity)*

H^+ + CO_3^{-2} ⇔ HCO_3^-



Net effect of high CO_2

Increasing HCO_3^-

Lowering CO_3^{-2}

Lowering pH

Acid-Base Reactions, pH, etc.

An example of acid-base reaction is dissociation of water into ions:

$$H_2O \rightleftarrows H^+ + OH^-$$

A pure water contains equal concentrations of hydrogen (H^+) and hydroxyle (OH^-) ions, (as the net charge must be neutral), and these concentrations can be derived from:

$$\frac{(H^+)*(OH^-)}{(H_2O)} = K \approx 1 * 10^{-14}$$

Since, at equilibrium, the molar amount *of* $(H^+) = (OH^-)$, and thus in pure water:

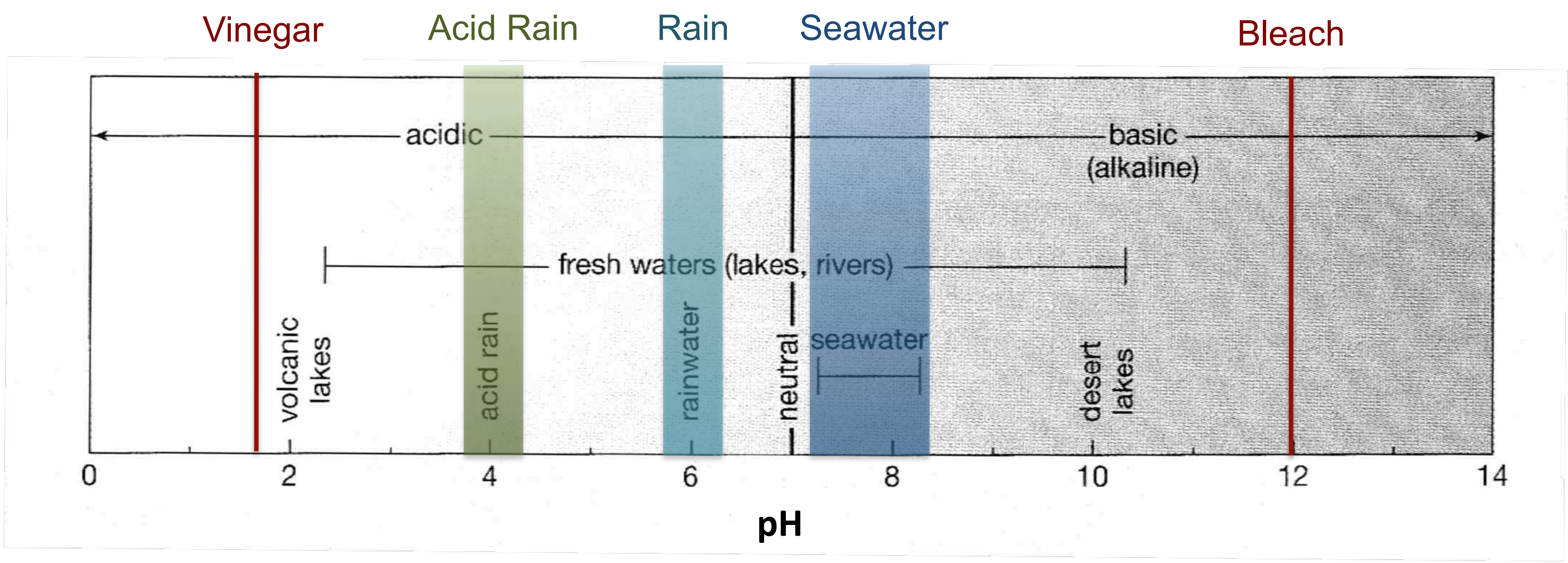
$$(H^+) = 1 * 10^{-7} \text{ mol/L}$$

For practical reasons, it is convenient to express the **concentration of (H^+) ions** as the **pH value**, defined by:

$$pH = -log_{10} (H^+)$$

Thus when (H^+) ion concentration of a solution is equal to $1*10^{-7}$ mol/L, its pH is 7

The pH Scale for Natural Waters



Acid is any substance that can donate a proton (i.e. H^+ ion) to another substance

Base is a substance that can accept a proton (H^+ ions) from another substance

Alkalinity measures the ability of a solution to neutralize acids (or H^+ ions), thus and an increase in pH (or H^+ ions) will decrease, or consume, the alkalinity

In seawater or groundwater, the alkalinity is mostly made up by the following species: **HCO_3^-, CO_3^{2-}** (carbonate ions), **$B(OH)_4^-$**, and **OH^-** (hydroxides) = **Total Alkalinity**

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Practicals: Determination of Carbonate Alkalinity via Acid-Base Titration

LECTURE 5: Arba Minch, Ethiopia, Oct 17, 2014

Determination of Alkalinity via Titration

The saturation state of seawater with respect to $CaCO_3$, and the capacity of the oceans to absorb anthropogenic carbon dioxide, are strongly dependent on the availability of CO_3^{2-} ions in the surface ocean waters.

In addition**, carbonate ions, CO_3^{2-}, are primary species in seawater that can neutralize acid, or H^+ ions**, thus protecting waters and its aquatic life from sudden shifts in pH caused by human-induced 'acidification'.

Alkalinity of water is a measure of how much acid (H^+ ions) it can neutralize, and because CO_3^{2-} ions are primary constituents we report alkalinity in units of mg/L of $CaCO_3$, and it is **determined via titration**

Titration is any reaction in which the amount of one reactant (in our case acid) is monitored volumetrically.

The objective of an acid-base titration is to determine the 'neutralization point', known also as '**equivalence or inflexion point**', and for our alkalinity titration it will be at pH of about 4.5.

Alkalinity titration curve is used to determine the position of an 'equivalence point', which in turn is used for the calculation of the alkalinity.

Determination of Carbonate Alkalinity via Acid-Titration

The main reaction occurring in this titration is

$$H_2SO_4 + CaCO_3 \longrightarrow H_2O + CO_2 + CaSO_4$$

Since the reaction of sulfuric acid with calcium carbonate has a stoichiometry of one to one, the following equality is valid at the equivalence point:

$$M_{H2SO4} \text{ x } V_{H2SO4} = M_{CaCO3} \text{ x } V_{CaCO3}$$

From the above equation we can calculate M_{CaCO3}

$$M_{CaCO3} \text{ (mol } CaCO_3\text{/L)} = (M_{H2SO4} \text{ x } V_{H2SO4})/V_{CaCO3}$$

(where V_{H2SO4} = value read from burette, M_{H2SO4}=0.0100 mol/L, V_{CaCO3}=100.0 mL)

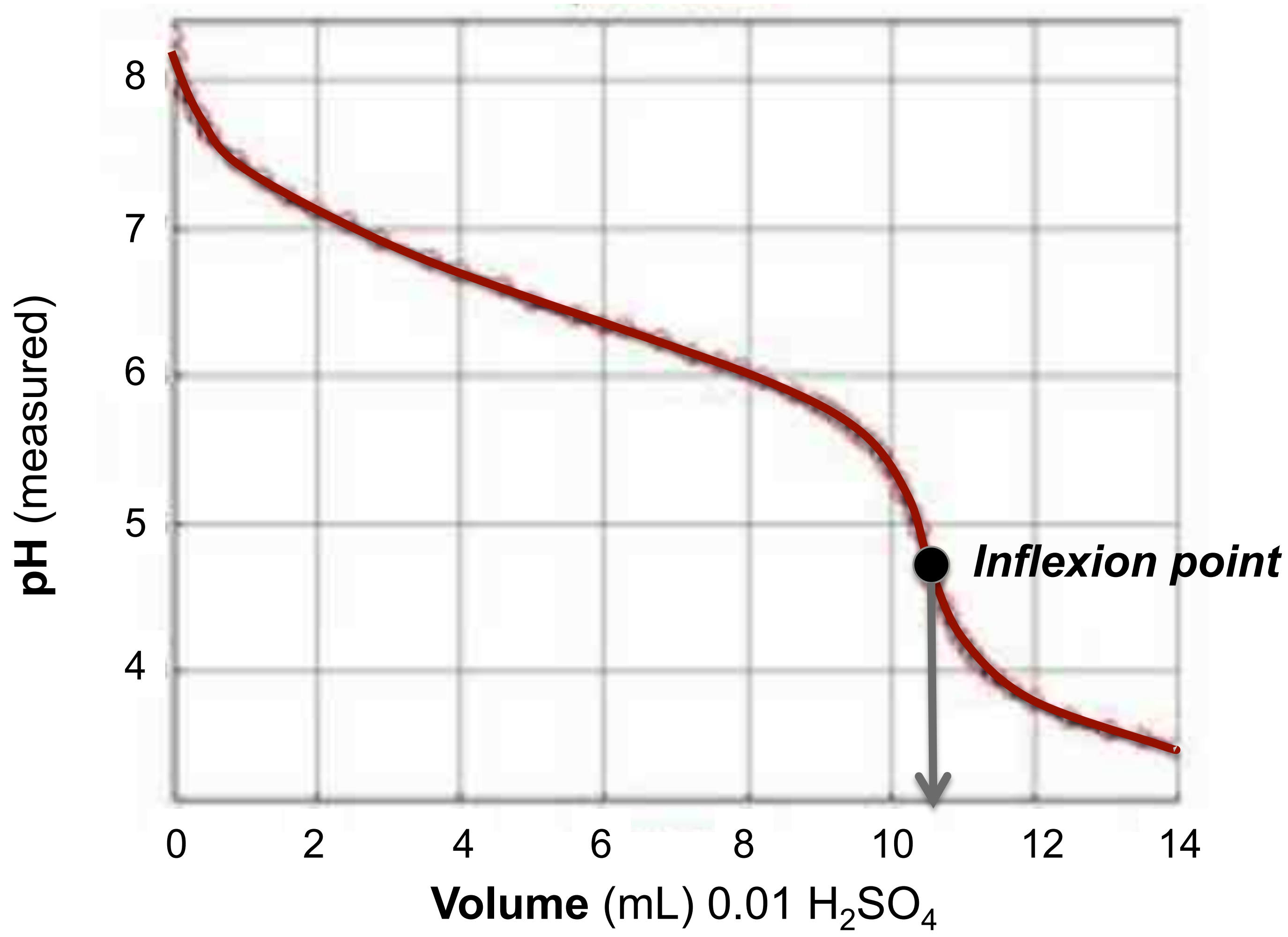
Acid: 0.01 M H_2SO_4

Base (water sample): 100 mL

Alkalinity (in mg/L $CaCO_3$) can then be calculated from M_{CaCO3} (mol $CaCO_3$/L) and the molar mass of $CaCO_3$ (100 g/mol) as follows:

$$\text{Alkalinity} = (\text{mol } CaCO_3\text{/L}) \text{ x } (100 \text{ g / 1 mol } CaCO_3) \text{ x } (1{,}000 \text{ mg / 1 g}) = \text{mg/L } CaCO_3$$

Alkalinity Titration Curve



If you plot the pH versus the volume of acid that was added, and draw a smooth curve, a graph similar to the one shown in Figure 1 will result. The inflexion point in the graph (the steepest drop in pH) gives the equivalence point of the titration. If, from the inflexion point, you drop a perpendicular down to the volume of acid axis, you can determine the volume of acid (mL) needed to neutralize the basic ions in your sample.

Earth System Perspective on Global Carbon Cycle

LECTURE 5: Arba Minch, Ethiopia, Oct 17 to 23, 2014

The Concept of Cycling in Earth System Science

Spatial and temporal hierarchy of earth system processes

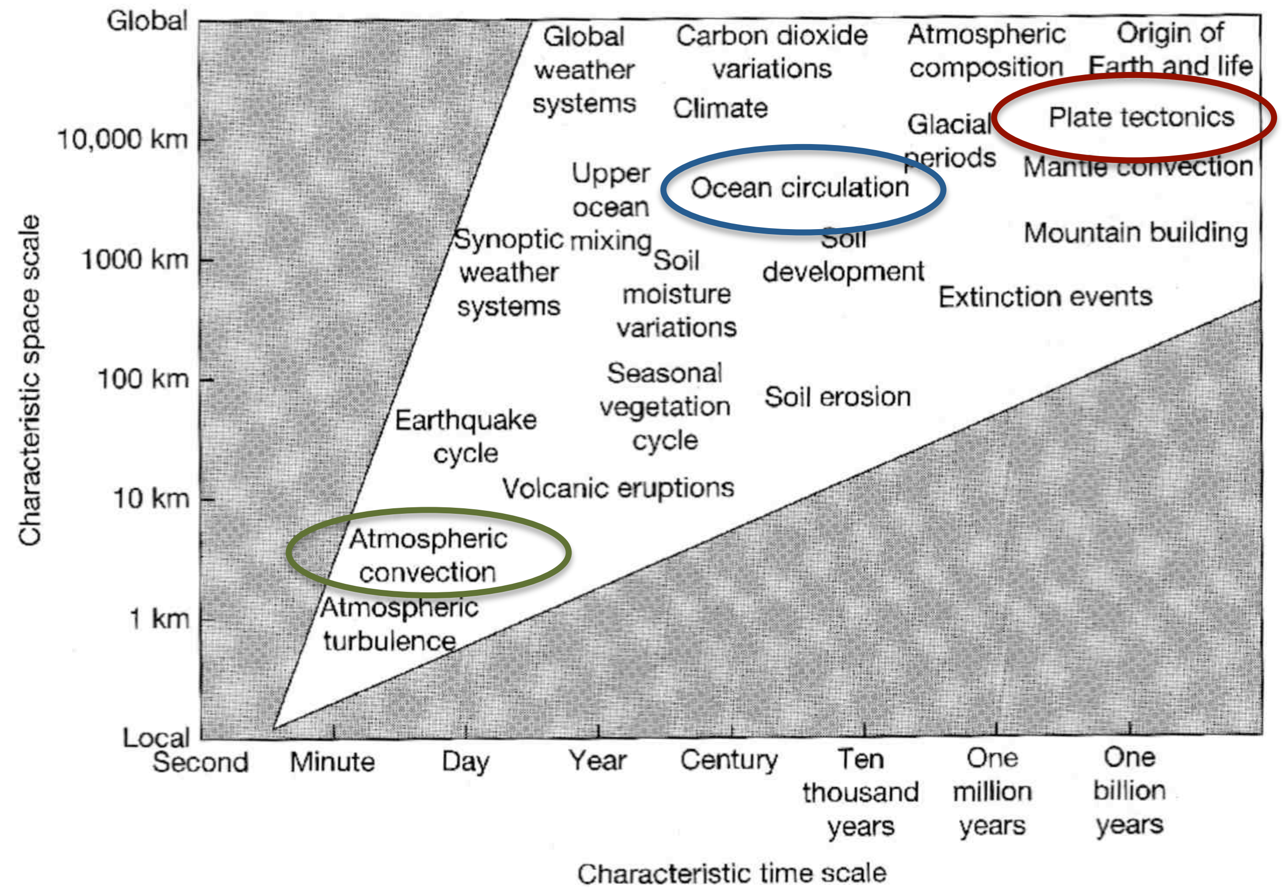


FIGURE 1.2 Earth system processes grouped according to their space and time scales. The space scale is logarithmic and the time scale is relative. (*Source:* Graedel and Crutzen, 1993.)

Basic Concepts in Earth System Science

EARTH SYSTEM is a 'complex' system characterized by processes that often switch from one state to another by natural evolution, or by "feedbacks"

A 'FEEDBACK' is a process or mechanism that either amplifies (positive feedback) or diminishes (negative feedback) the magnitude of a perturbation to a system.

A system may have STABLE (equilibrium) set points, or the system may exist in UNSTABLE state in which a slight disturbances may cause the system to change dramatically.

These are TIPPING POINTS of the system and are of great interest today in terms of phenomena such as global warming and ocean acidification

Tipping point

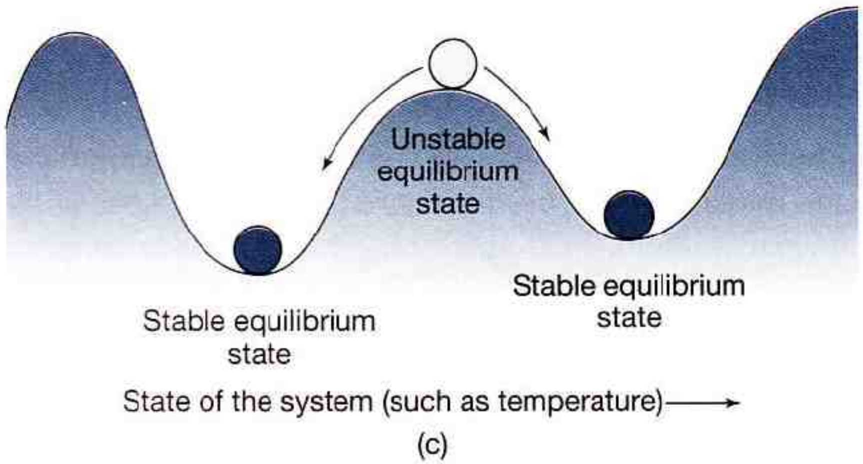


FIGURE 2-3 The equilibrium states of a system, represented as peaks (unstables) and valleys (stables). On disturbance, the system returns to stable equilibrium states but moves away from unstable equilibrium states.

The Global Carbon Cycle – Schematic Diagram

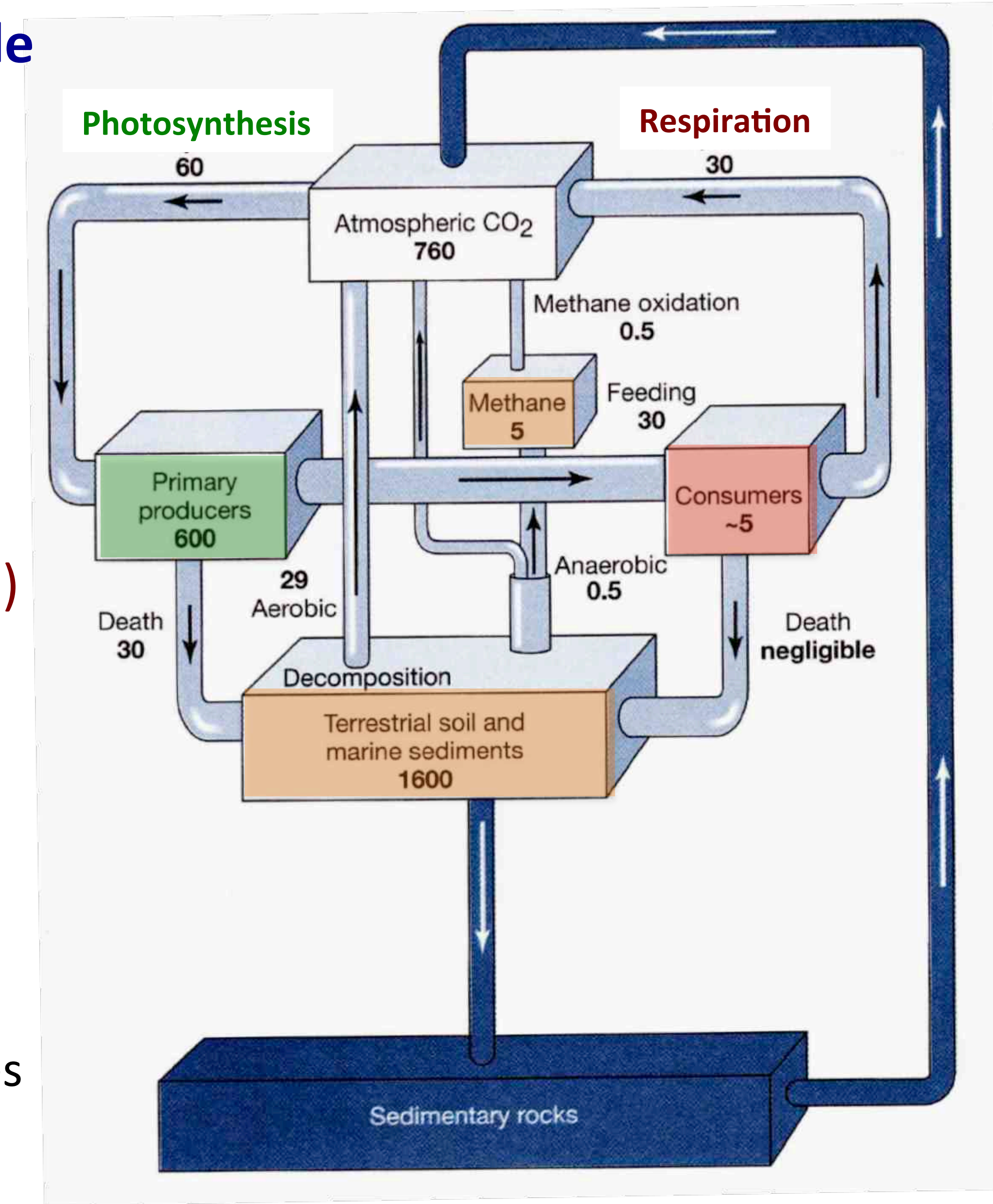
Short-Term Organic Carbon Cycle

This sub-cycle involves processes that operate on a daily to seasonal time scale, such as **respiration** and **photosynthesis** by plants and algae

Primary producers (plants) are responsible for the photosynthetic processes, and **consumers** (animals) contribute to respiration CO_2 fluxes

Furthermore, **methanogenesis** also contributes to the inflow CO_2 fluxes:

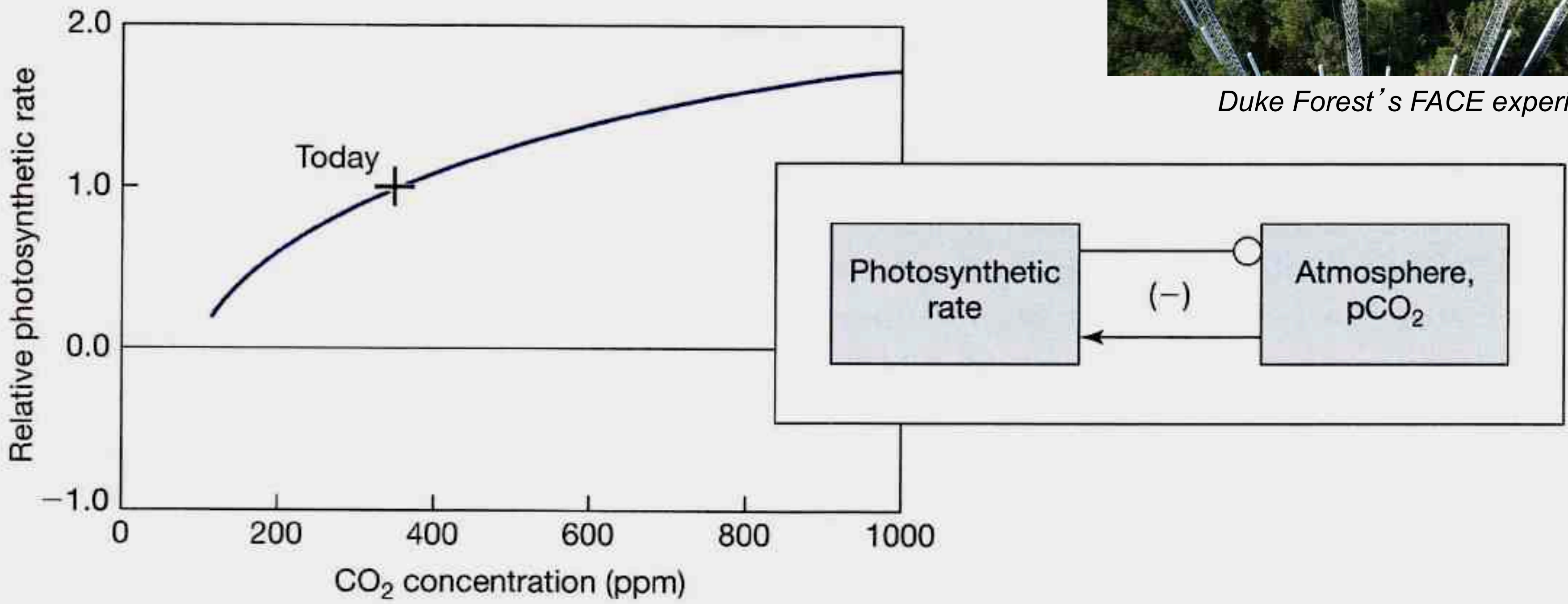
$2CH_2O \Rightarrow CO_2 + CH_4$ *(methane)*
it is **anaerobic respiration** by microbes in the oxygen-depleted environments



The CO_2 Fertilization Effect:

A negative feedback between the photosynthetic rate of plants and the atmospheric CO_2 levels.

Duke Forest's FACE experiment

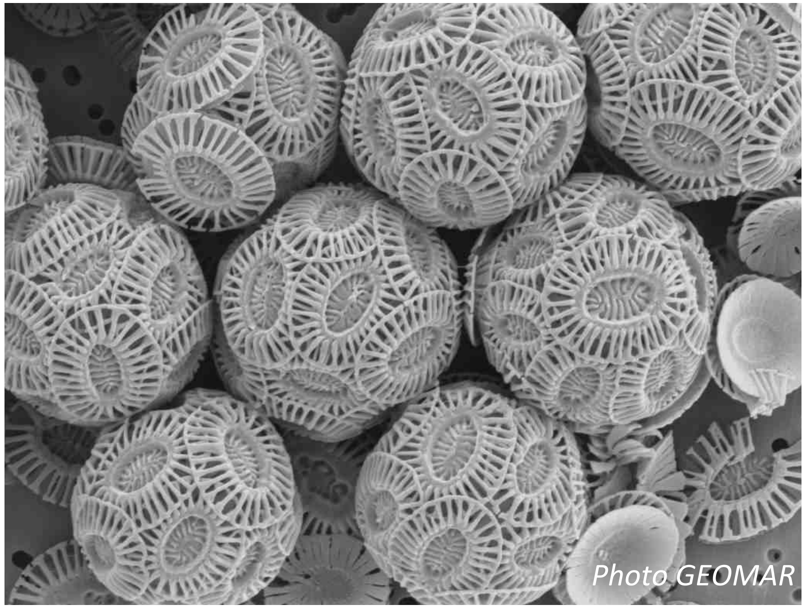


As CO_2 levels go up, plants photosynthesize more rapidly (***the CO_2 fertilization***). But as they grow faster, CO_2 tends to fall, because it is consumed by plants during the photosynthesis. Thus terrestrial biota tend to stabilize the atm. CO_2 levels.

Short-Term Organic Carbon Cycle – Marine Environment

The dominant primary producers in the oceans are free-floating, photosynthetic marine micro-organisms, **phytoplankton**, mainly ***diatoms and coccoliths (algae)***

Diatoms – a group unicellular marine algae organisms (phytoplankton) that form their tiny shells from SiO_2



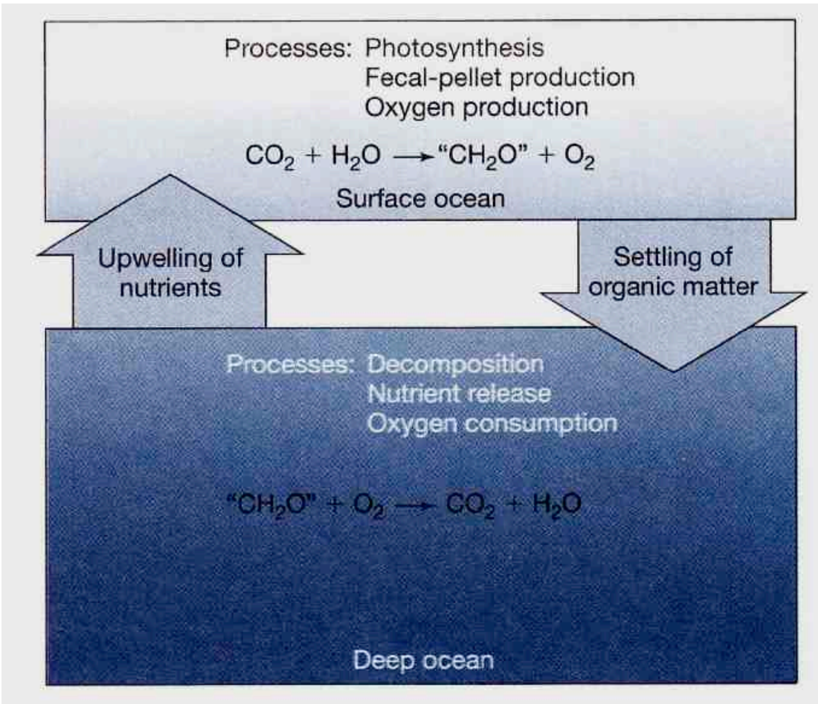
Coccolithophores – single-celled marine algae (phytoplankton) with shells formed by $CaCO_3$

These **marine phytoplankton species consume CO_2 and produce O_2** through the photosynthesis, in much the same way as do the terrestrial (land-based) plants

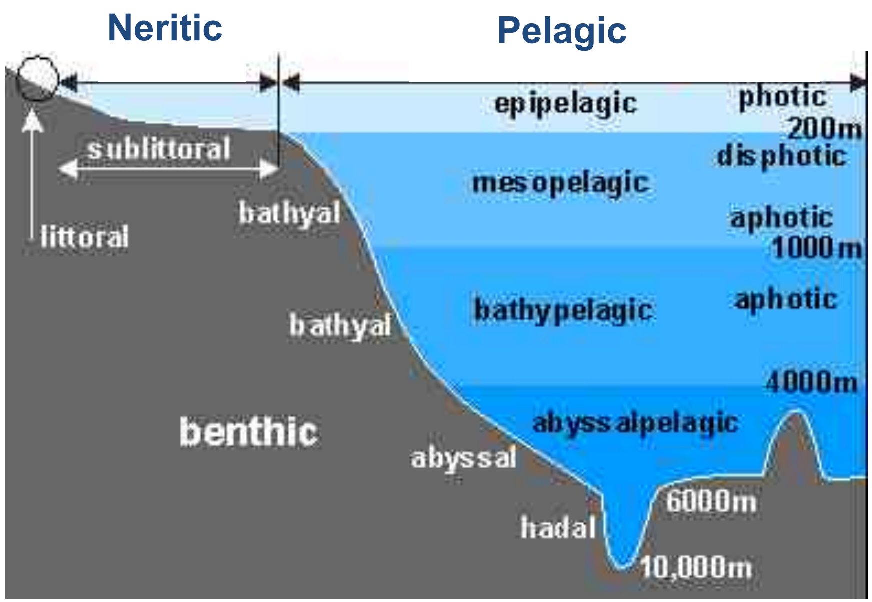
The Marine Organic Carbon Cycle

The Biological Pump - is the process by which CO_2 fixed during the photosynthesis by marine phytoplankton (*diatoms, coccoliths*) is removed and transferred from the surface ocean (i.e. *photic zone*) to deeper parts by gravitational settling of decayed phytoplankton-derived organic matter

The Marine Biological Pump



Major Oceanic Zones and Provinces

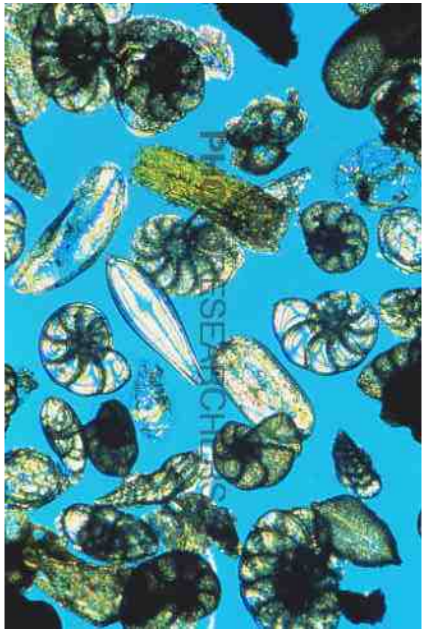


The Marine Organic Carbon Cycle

Much of the organic matter produced in the surface ocean by phytoplankton is consumed by **zooplankton**, i.e. free-floating marine consumers, including micro-organisms as ***foraminifera*** and ***radiolarians***, that cannot photosynthesize

Planktonic zooplankton

Radiolarians *(SiO_2 shells)*

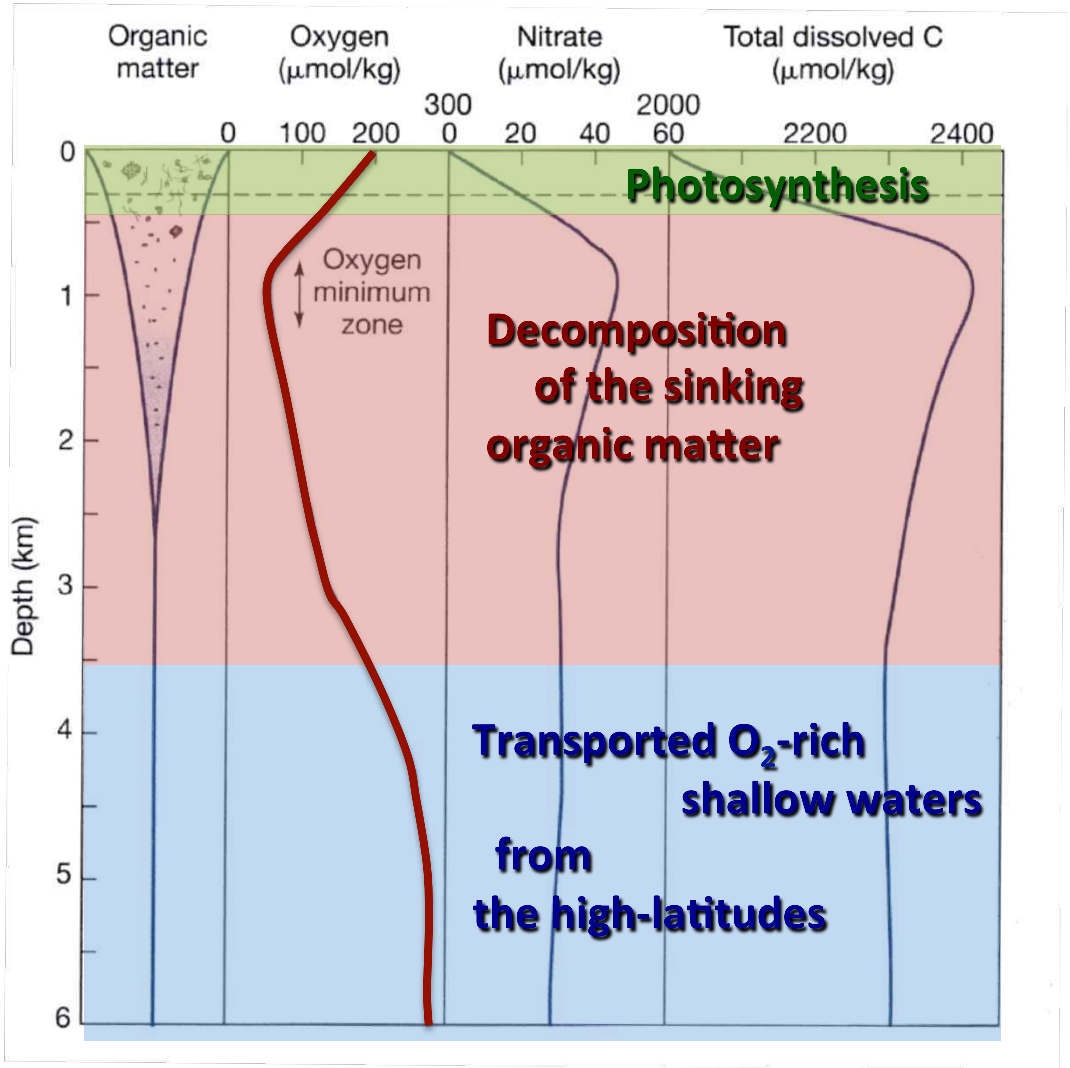


Foraminifera *($CaCO_3$ shells)*

Decayed organic matter derived from zooplankton contributes significantly to the 'biological pump' and net export flux of carbon from shallow to deep waters

The Marine Organic Carbon Cycle

The Oxygen Minimum Zone (OMZ)



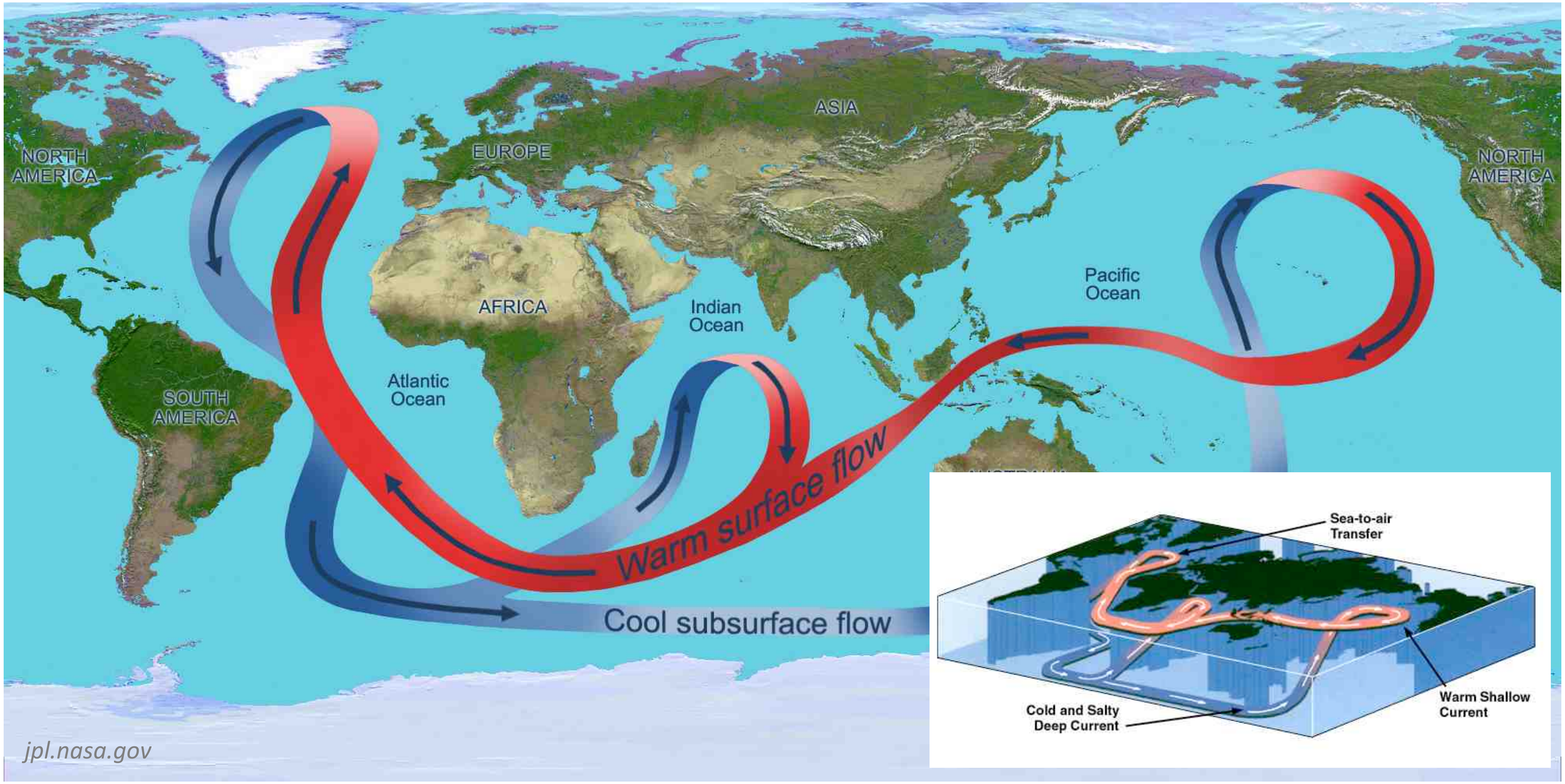
The decomposition of plankton-derived organic matter settling through the water column will consume oxygen, creating an **oxygen minimum zone (OMZ)**

In this zone, dissolved O_2 levels reach a minimum as a result of high oxygen demand by aerobic decomposers and low O_2 supply from the surface ocean.

Below the OMZ, the levels of O_2 increase again, due to presence of deep O_2-rich waters, which originated at high-latitude shallow depths and were transported here via the global ocean circulation

Global Ocean Circulation

The Global Ocean Conveyor Belt



An idealized map of ***warm surface water flow*** *(red)* and the returning circulation of the ***deep O_2-rich waters*** *(blue)*, that define a pattern called a '**global conveyor belt**'

The Global Carbon Cycle

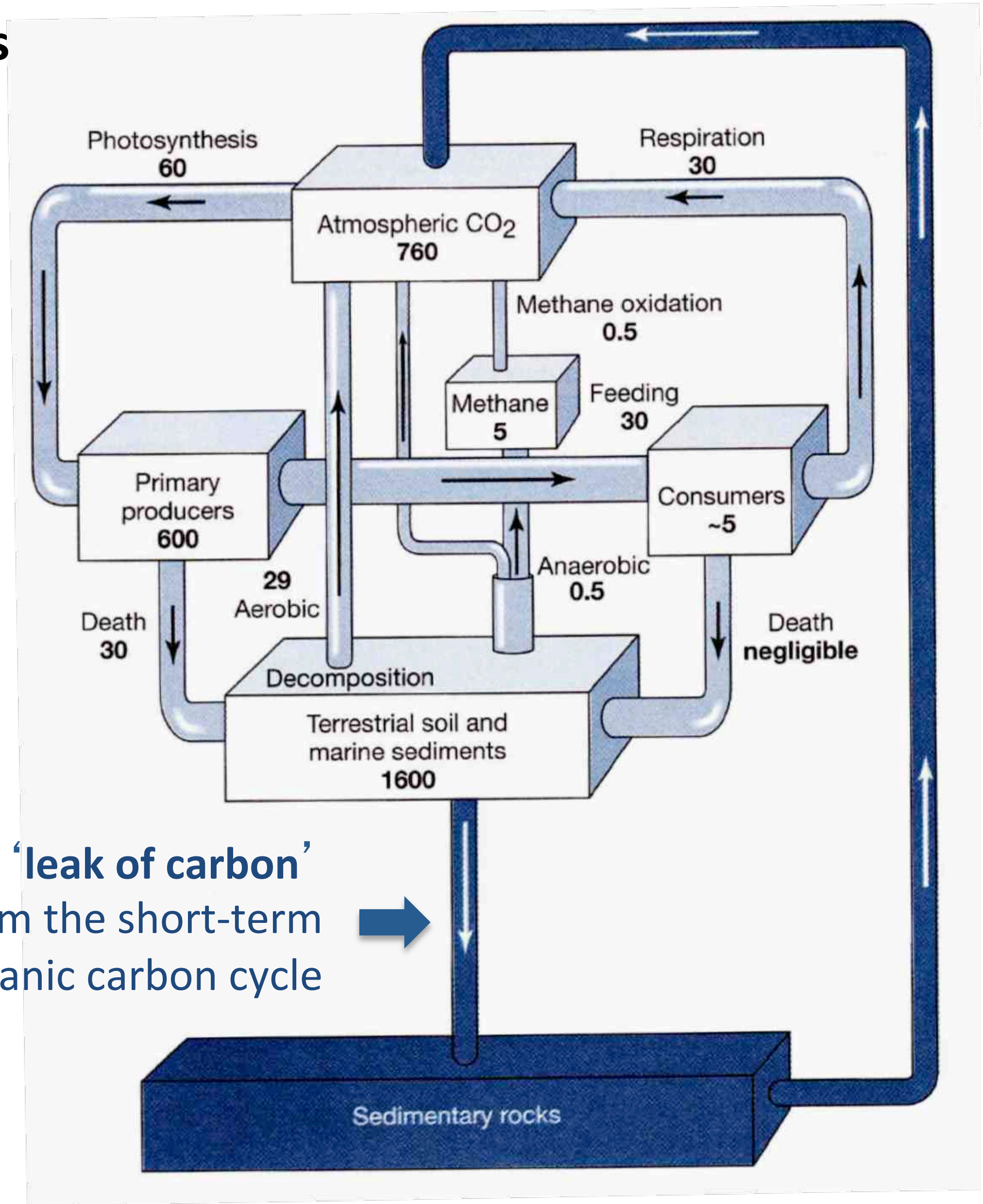
Carbon Burial in Sedimentary Rocks

This processes represents a ‘**leak of carbon**’ from the short-term organic carbon cycle, and it also **controls the levels of oxygen in the Earth’s atmosphere** over time

For every atom of C that enters this ‘sedimentary rocks’ reservoir in the form of organic matter (CH_2O), one O_2 molecule is left behind:

$$O_2 + CH_2O \Rightarrow CO_2 + H_2O$$

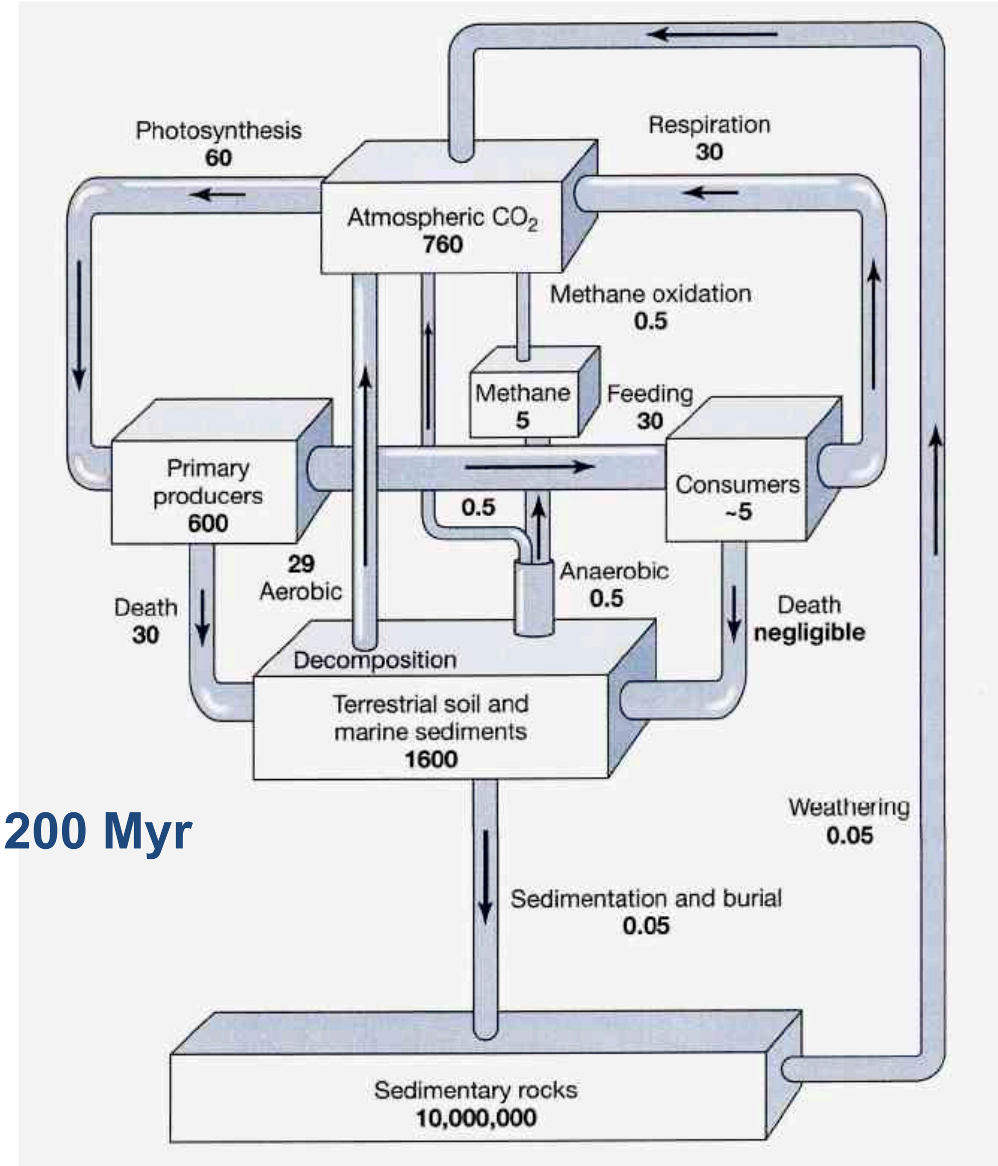
Because O_2 liberated during photosynthesis of carbon, is not utilized during decomposition of the buried organic matter (CH_2O)



The ‘**leak of carbon**’ from the short-term organic carbon cycle

Carbon Burial in Sedimentary Rocks

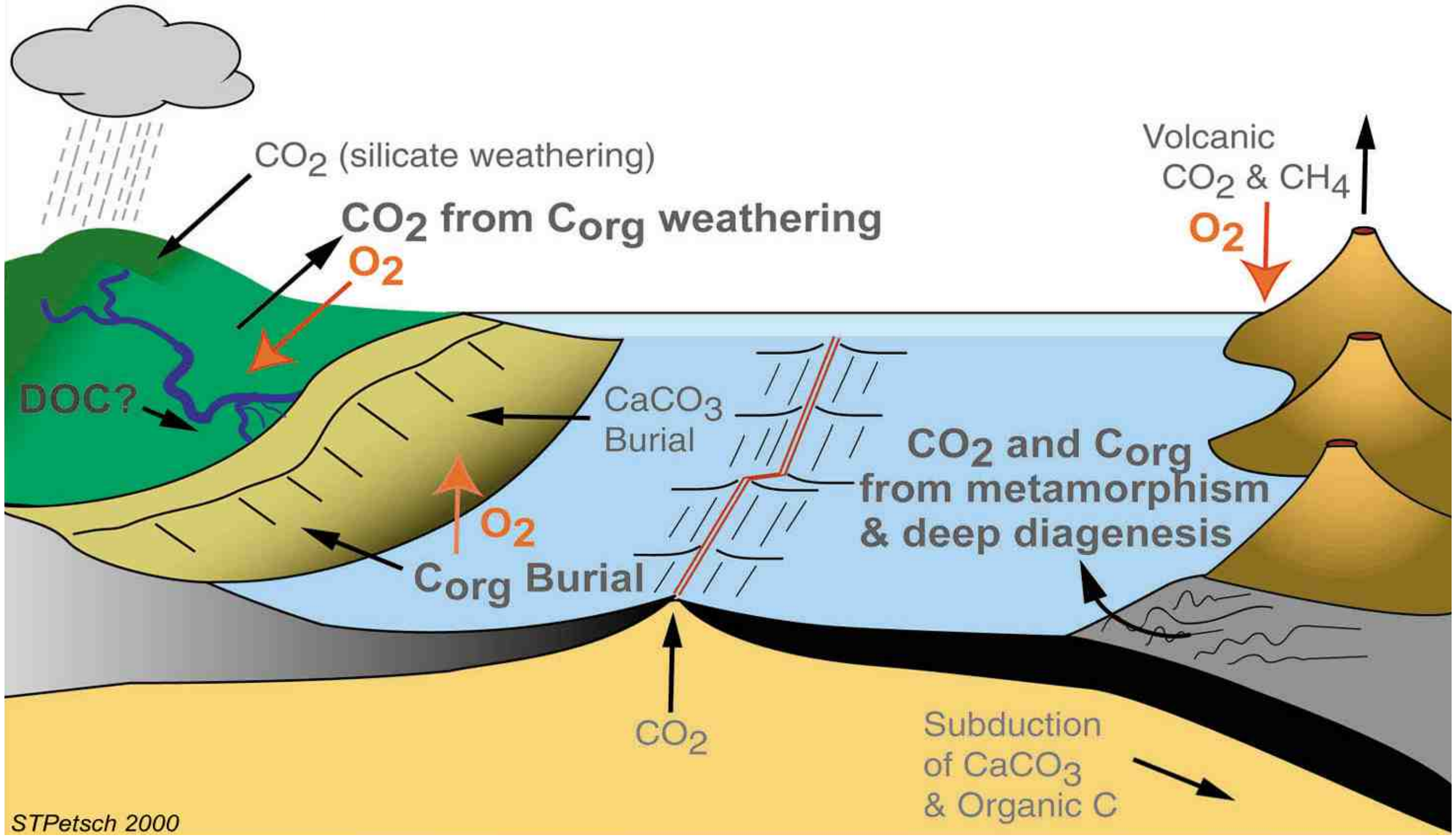
The fluxes of carbon involved in these processes (CH_2O burial) are small (0.05 Gt/yr) and the reservoirs are extremely large (10,000,000 Gt), and therefore these processes become important on longer geological timescales (millions of years).



$$\textbf{Residence time} = \frac{\textbf{10,000,000}\ \text{Gt(C)}}{\textbf{0.05}\ \text{Gt(C)/yr}} = \textbf{200 Myr}$$

In this sense, the extraction and combustion of fossil fuels (CH_2O), is just an acceleration of this natural process of oxidative C weathering

The Link between the Long-term Carbon and Oxygen Cycles



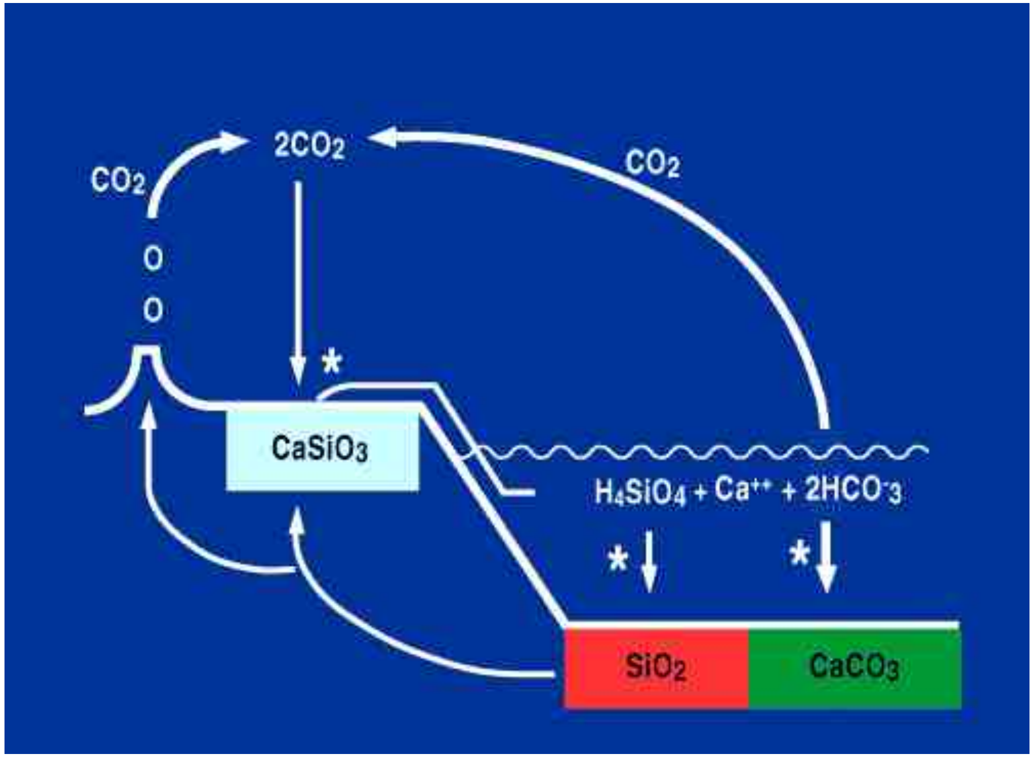
$O_2 + CH_2O \Rightarrow CO_2 + H_2O$ $\qquad$ $CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$

Global Carbon Cycle

The Inorganic Carbon Cycle

This sub-cycle is closely linked to the **silicate-carbonate cycle**, which supplies calcium (Ca^{2+}) and carbonate (HCO_3^-) ions to the oceans, where they react leading to the formation of $CaCO_3$, which is by far the largest reservoir of carbon on Earth's (40,000,000 Gt)

The Silicate-Carbonate Weathering Cycle

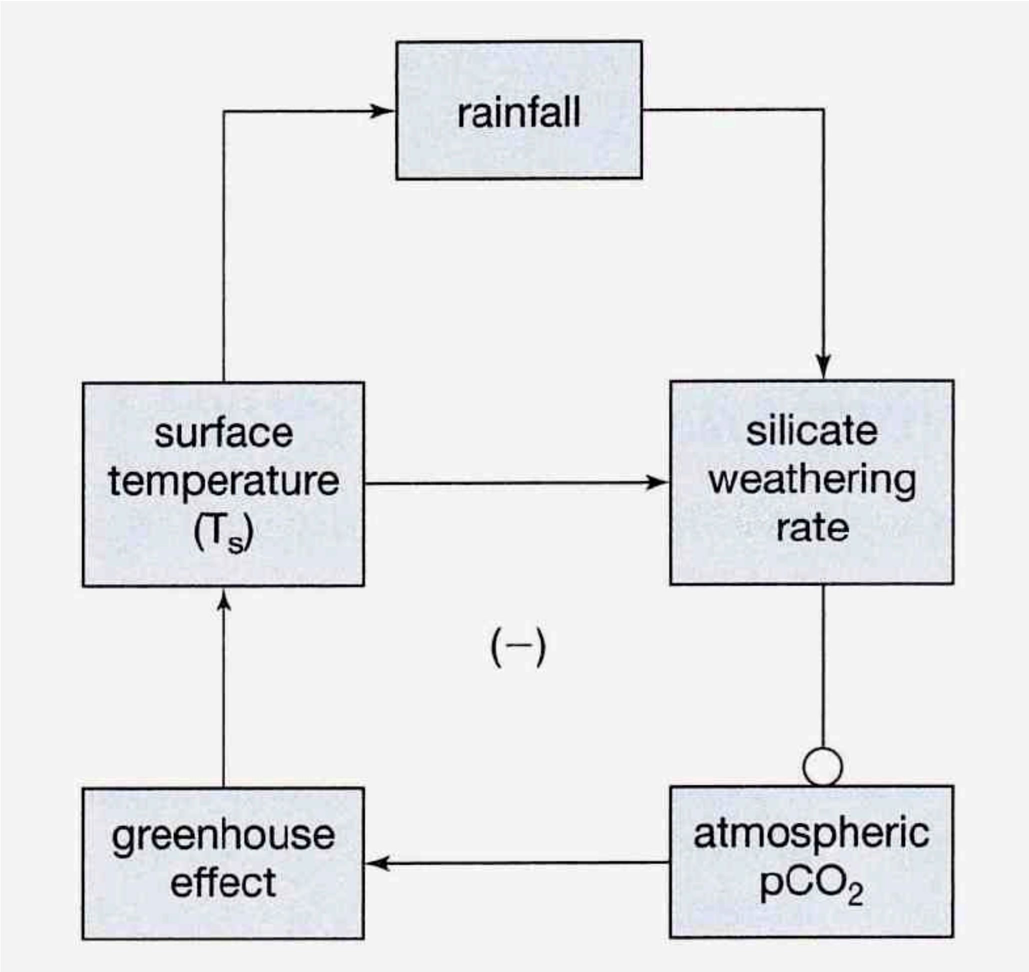


The Urey weathering reaction:

$$CO_2 + CaSiO_3 \underset{\text{(metamorphism)}}{\overset{\text{(weathering)}}{\rightleftarrows}} CaCO_3 + SiO_2$$

The Inorganic Carbon Cycle

Negative Feedback of Silicate-Carbonate Cycle on Climate



>> higher atm. CO_2 levels

>> higher surface temperatures

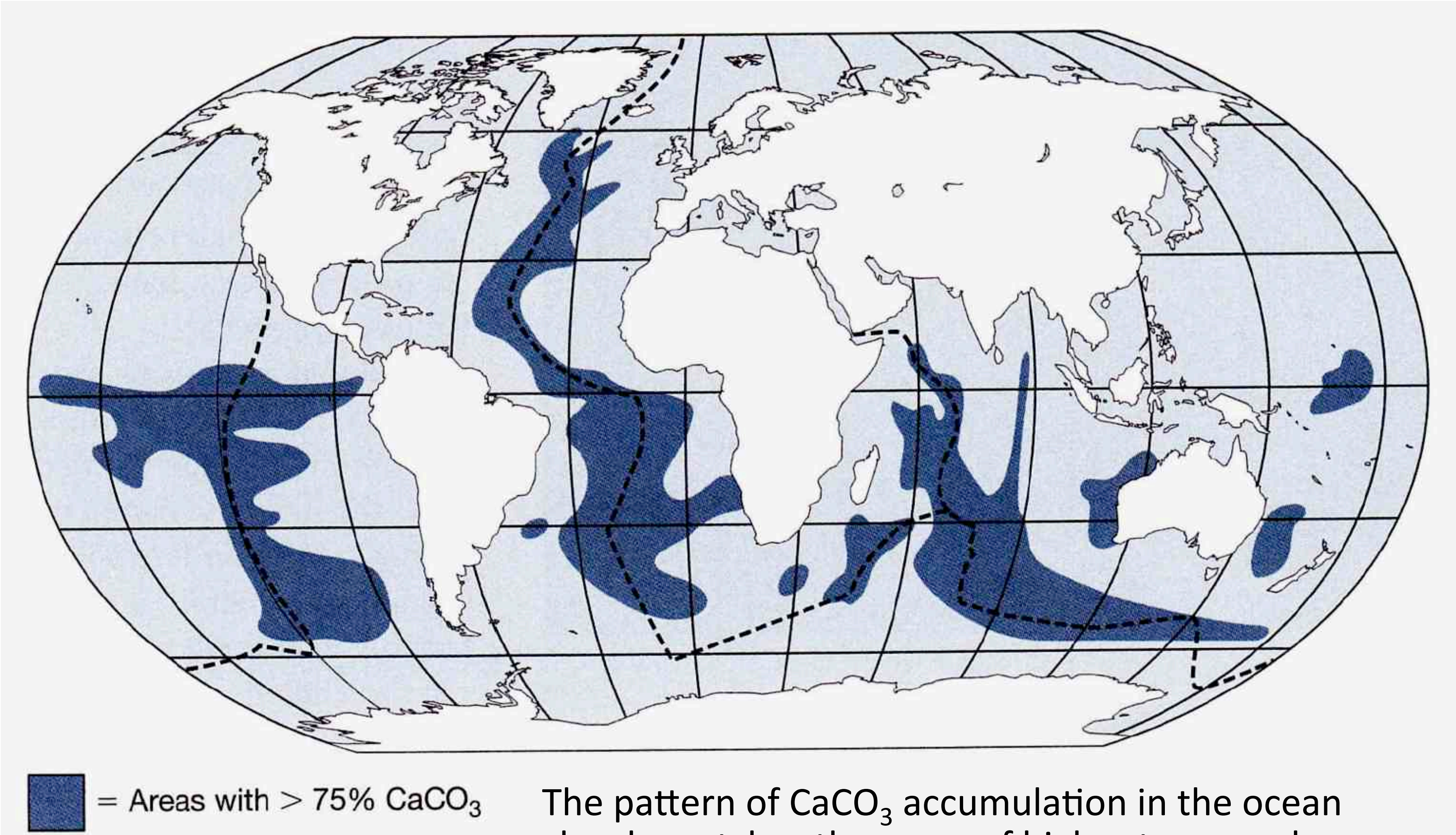
>> higher weathering rates

>> higher consumption of CO_2

This negative feedback loop is the major factor that has regulated atmospheric CO2 levels and thus the Earth's climate on longer time scales.

The Inorganic Carbon Cycle

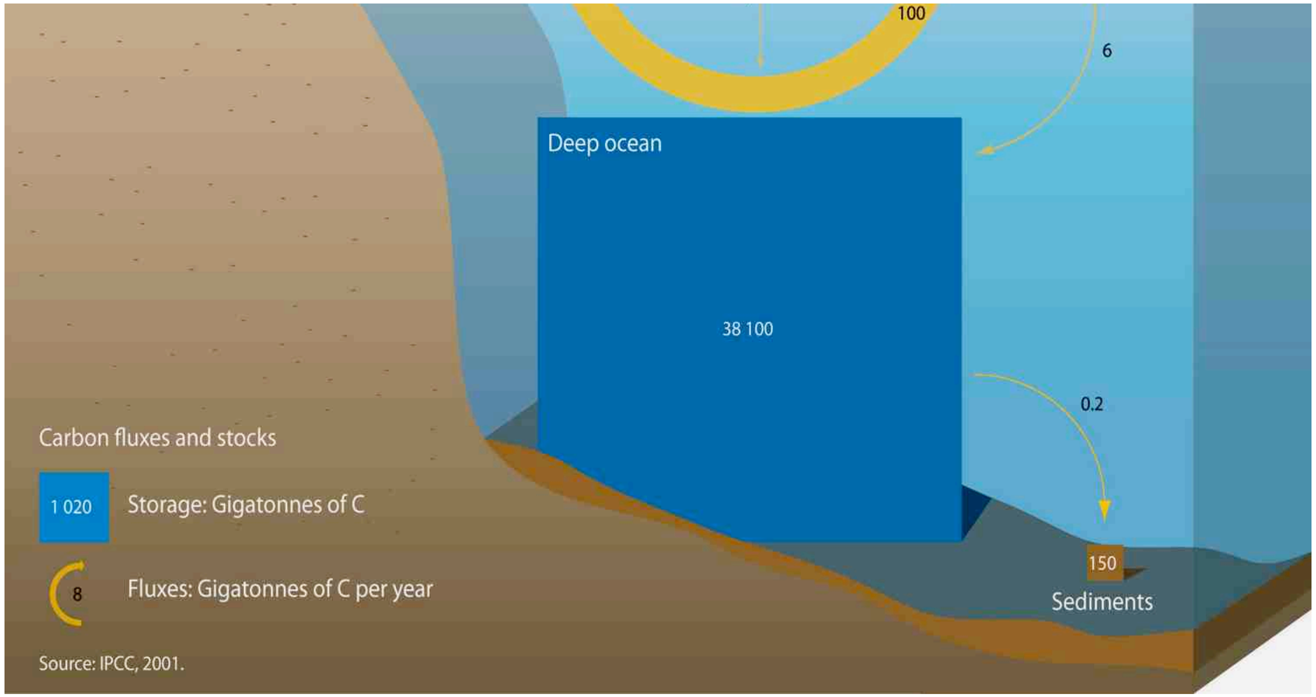
Pattern of Carbonate Mineral ($CaCO_3$) Deposition in the Global Ocean



The pattern of $CaCO_3$ accumulation in the ocean closely matches the areas of higher topography (shallow waters) situated along mid-ocean ridges

Carbon Exchange between Ocean and Atmosphere

"We are conducting a great geochemical experiment, unlike anything in human history and unlikely to be repeated again on Earth. Within a few centuries we are returning to the atmosphere and oceans the concentrated organic carbon stored in sedimentary rocks over hundred of millions of years" (Revelle and Suess, 1957; Houghton, 2005).



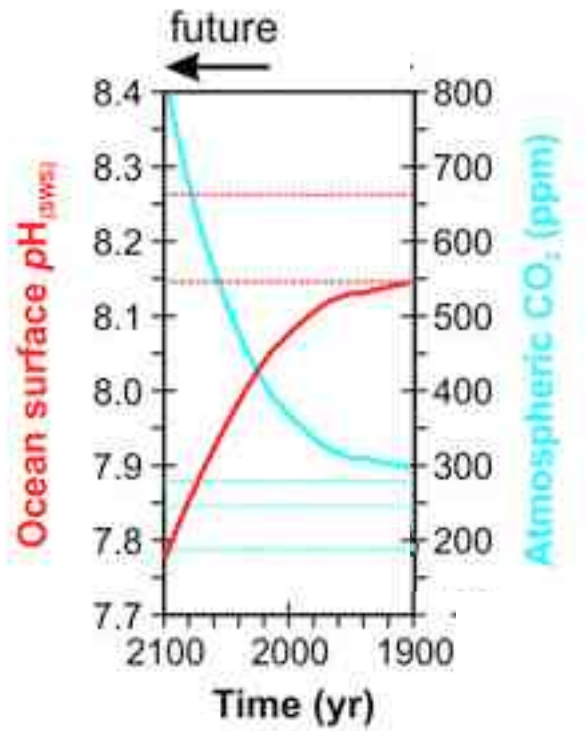
Where does anthropogenic CO_2 emissions go? (Sinks)

Oceans take up …………30%
Terrestrial Biosphere....20%
Atmosphere……………..50%

So only about half of the anthropogenic CO_2 remains in the atmosphere, and the rest is taken by oceans and vegetation on land !

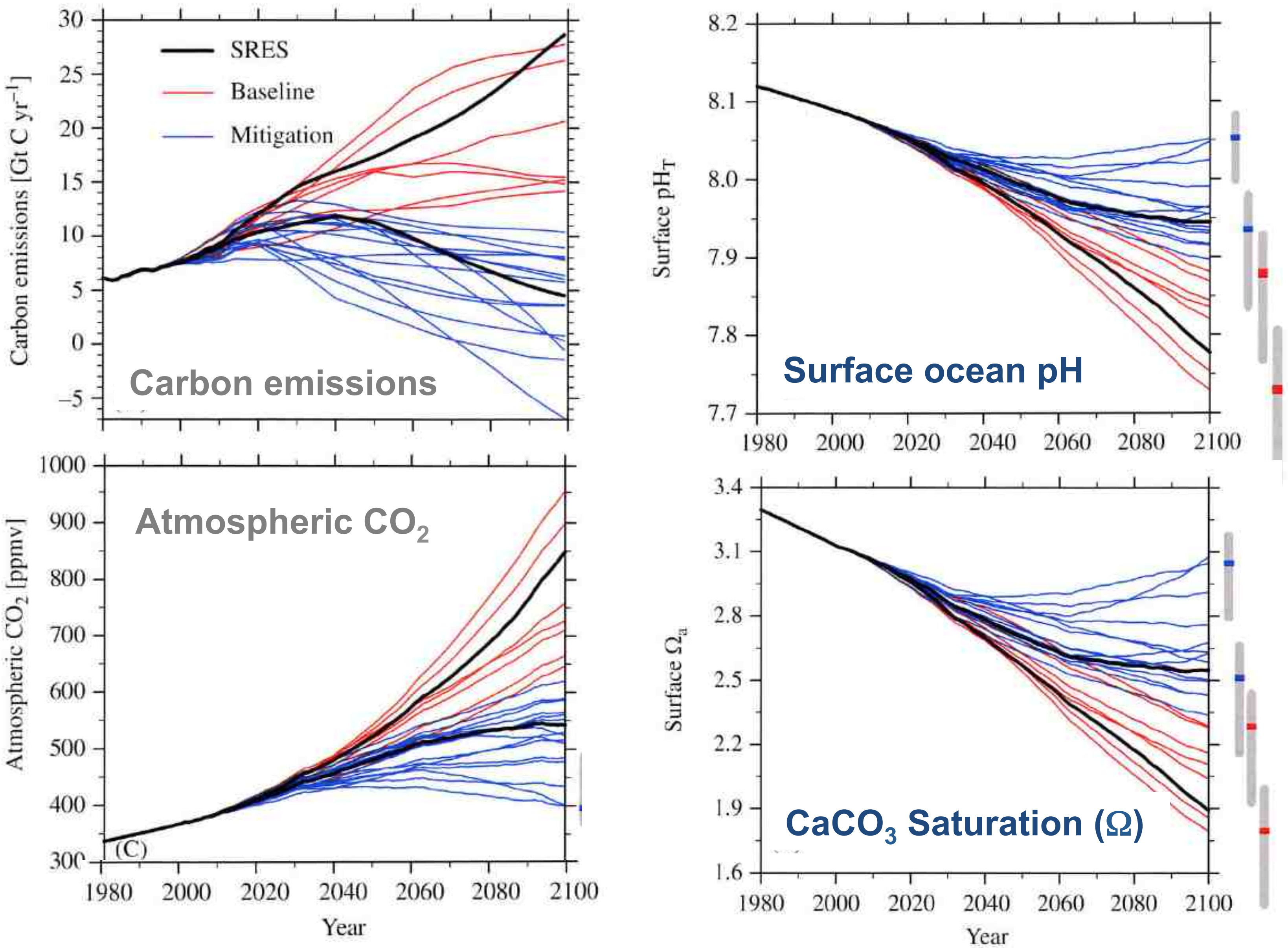
Recent changes in seawater pH due to ‘Ocean Acidification’

pH	H+ (moles per liter)	change in acidity
7.2	6.3×10^{-8}	+900%
7.3	5.0×10^{-8}	+694%
7.4	4.0×10^{-8}	+531%
7.5	3.2×10^{-8}	+401%
7.6	2.5×10^{-8}	+298%
7.7	2.0×10^{-8}	+216%
7.8	1.6×10^{-8}	+151%
7.9	1.3×10^{-8}	+100%
8.0	1.0×10^{-8}	+58%
8.1	7.9×10^{-9}	+26%
8.2	6.3×10^{-9}	

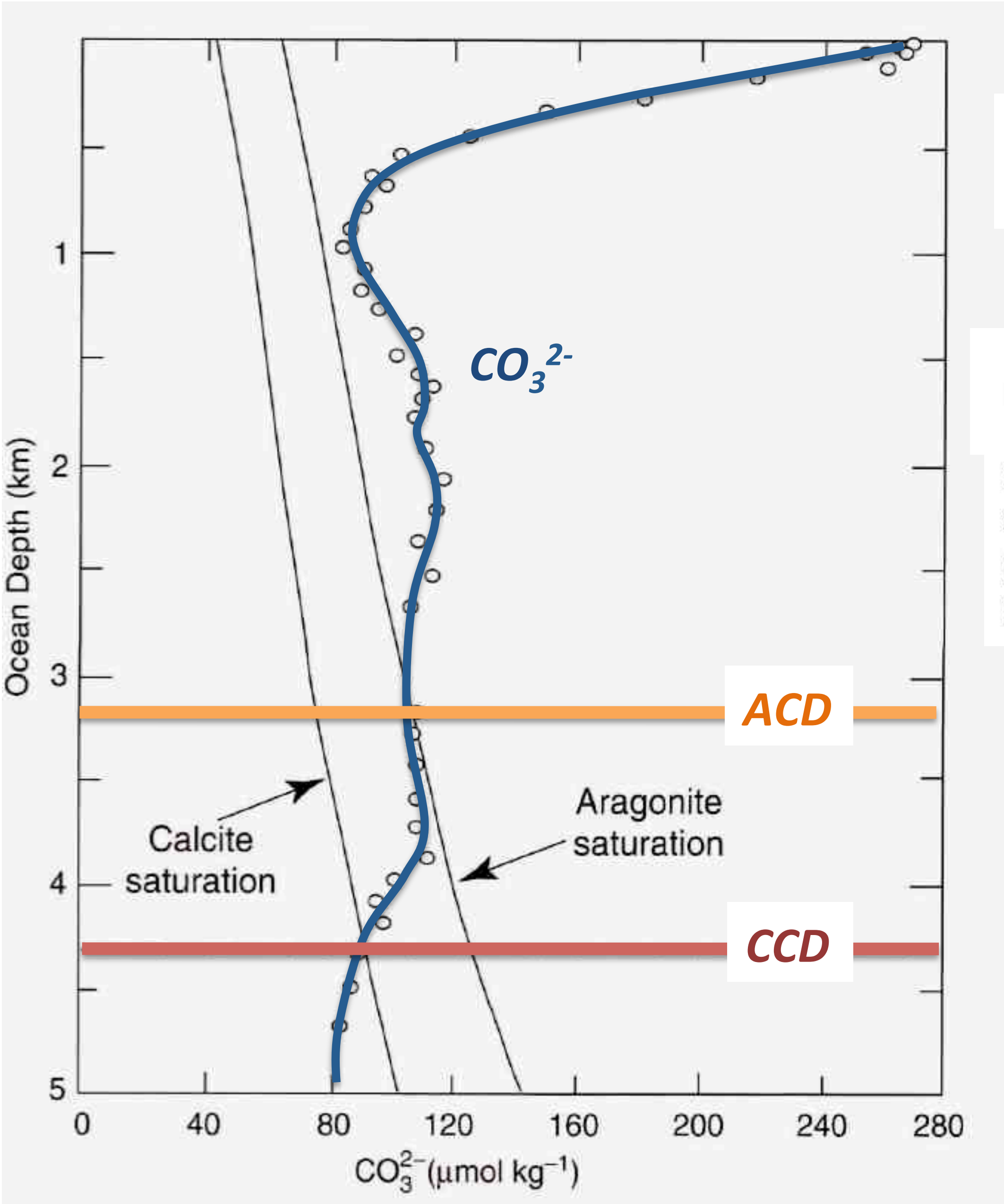


Based on geological record of the CO_2/pH calibration, one can predict that **by 2100, the acidity of oceans can increase by 150%**

Ocean Acidification Predictions (after Gattuso & Hansson, 2011)



Saturation of $CaCO_3$ Minerals in the Ocean



Precipitation/Dissolution

$$CaCO_3 = Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Saturation State (Ω)

$$\Omega = [Ca^{2+}][CO_3^{2-}] / K^*_{sp}.$$

Seawater is in equilibrium with that mineral when $\Omega = 1$, supersaturated when $\Omega > 1$ (which promotes inorganic precipitation), and is undersaturated when $\Omega < 1$ (which promotes inorganic dissolution).

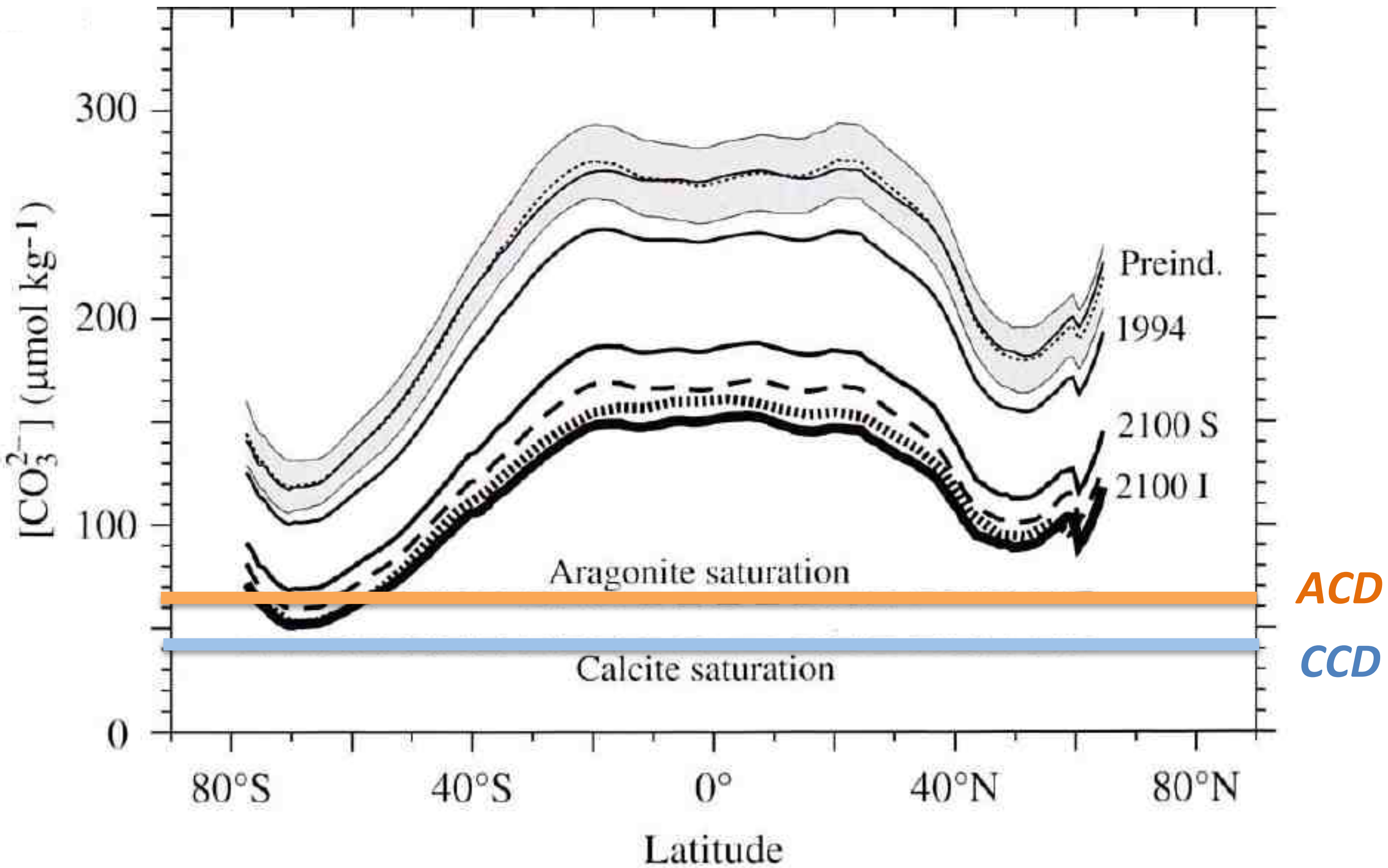
ACD *(Aragonite Compensation Depth)*

CCD *(Calcite Compensation Depth)*

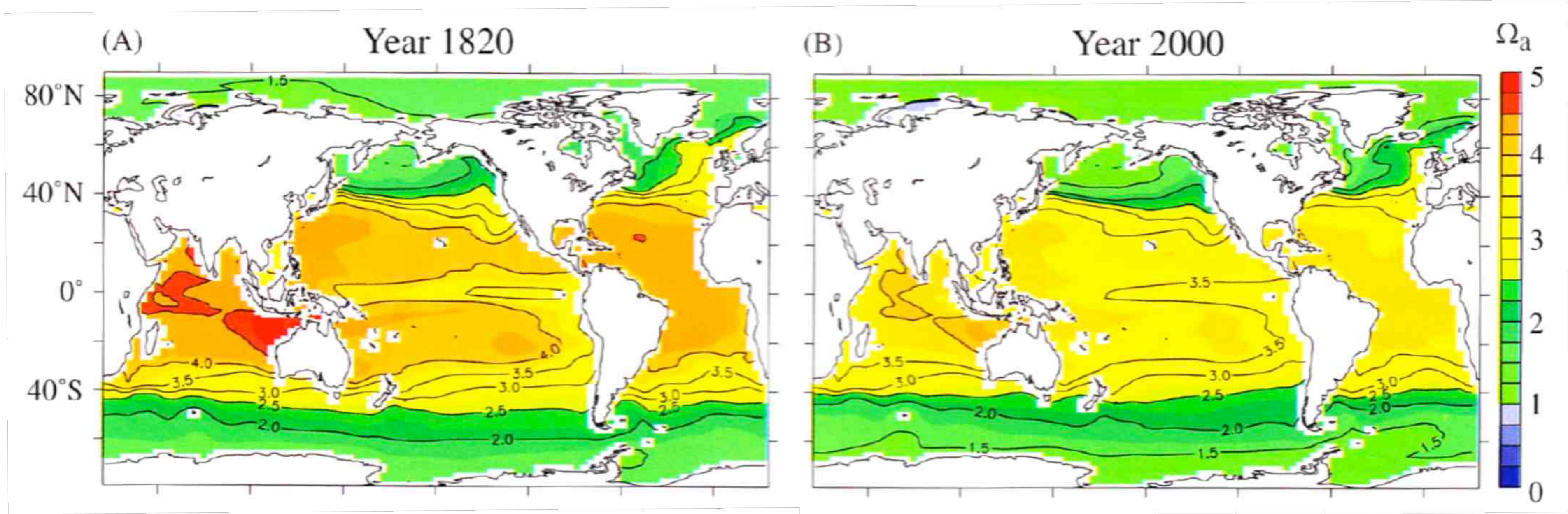
It is the depth below which seawater is under-saturated with respect to calcite, means that any $CaCO_3$ (calcite minerals) will dissolve below this depth (ca. 4300 m)

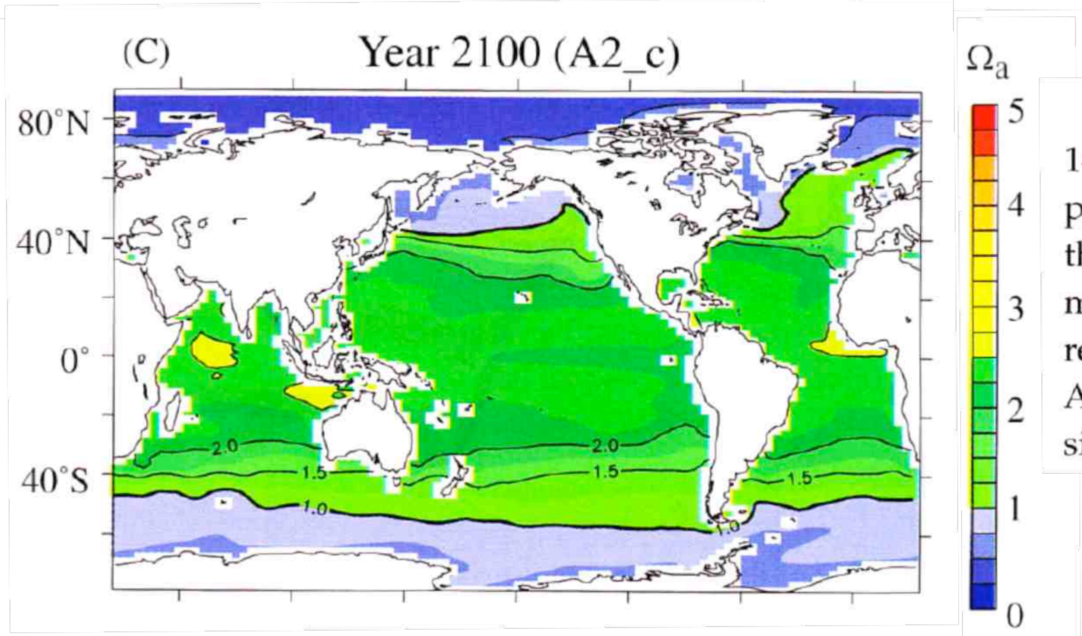
Saturation of $CaCO_3$ Minerals in the Ocean

Spatial Distribution of CO_3^{2-} concentrations in Global Ocean



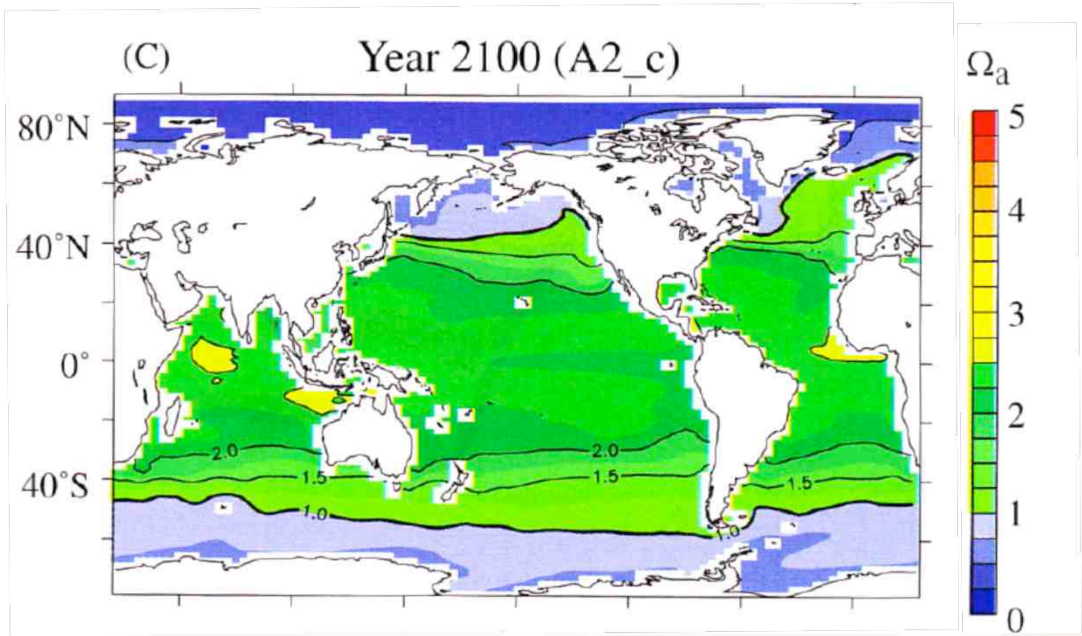
Aragonite Saturation of the Global Ocean (Gattuso & Hansson, 2011)





Undersaturation in the Arctic is imminent (Fig. 14.6C). By the time atmospheric CO_2 exceeds 490 ppmv (in 2040 in the 'A2_c' case), more than half of the Arctic Ocean will be undersaturated (annual mean; Steinacher *et al.* 2009). Undersaturation with respect to aragonite remains widespread in the Arctic Ocean for centuries even after cutting emissions in 2100 for both the 'A2_c' and the 'B1_c' cases

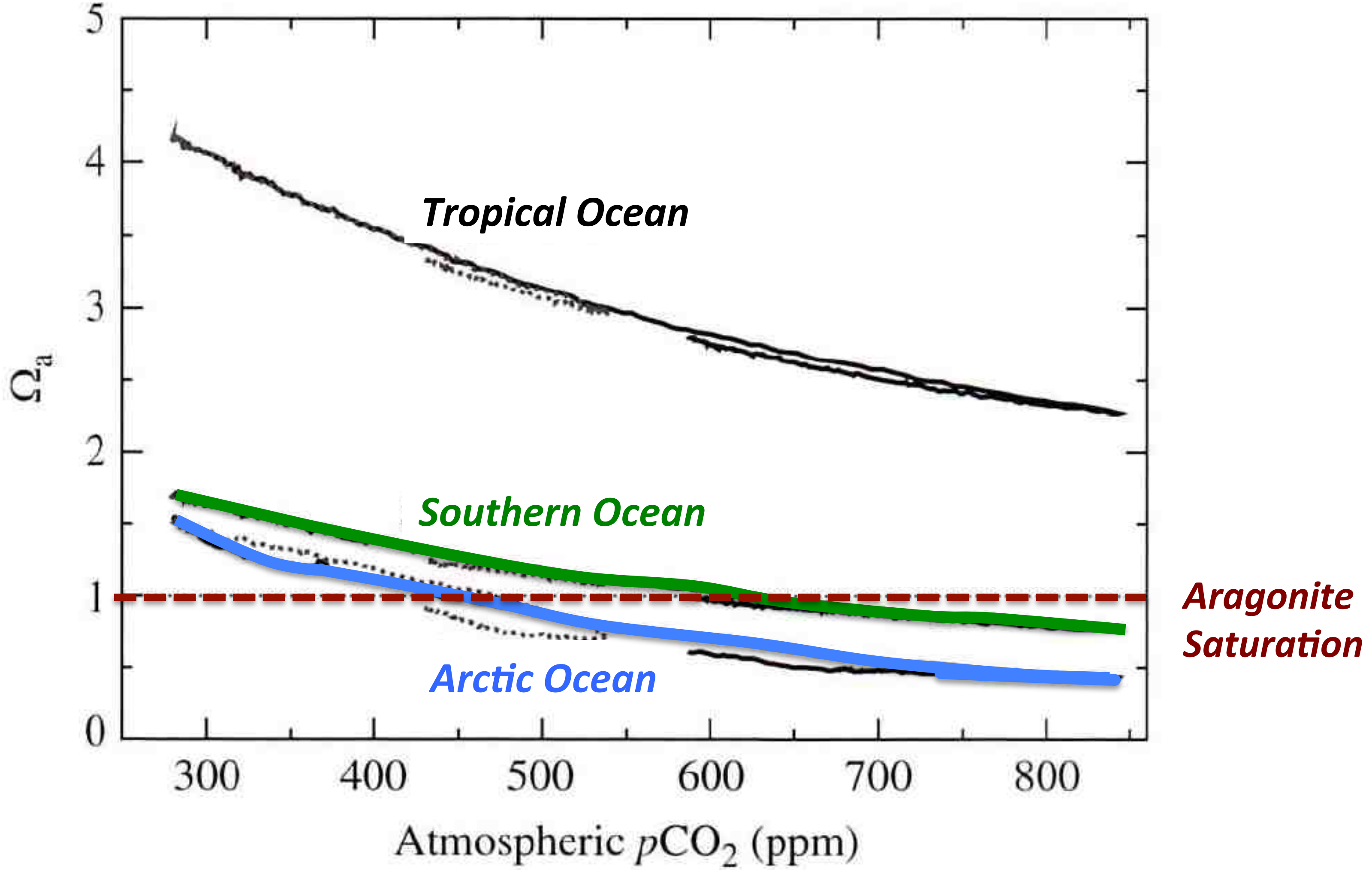
Environmental Issues Linked to Under-Saturated Arctic Oceans



Arctic zooplankton as **pteropods**, which make shells from aragonite, will be most affected by acidification

Pteropods are major food source in the Arctic for organisms ranging in size from tiny krill, to juvenile salmon and whales. The photos above show what happens to a pteropod's shell when placed in sea water with pH and carbonate levels projected for the year 2100. The shell slowly dissolves after 45 days (Gattuso and Hansson, 2011).

Future of 'Ocean Acidification' in the Global Oceans



Gattuso and Hansson, 2011