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The Global Carbon Cycle

Recording the Evolution of Earth, from the origin of life to the industrialization of the planet

Celebrating 5 years of world-leading collaborative and multidisciplinary research

2010 - 2015

BRISTOL 2015 EUROPEAN GREEN CAPITAL

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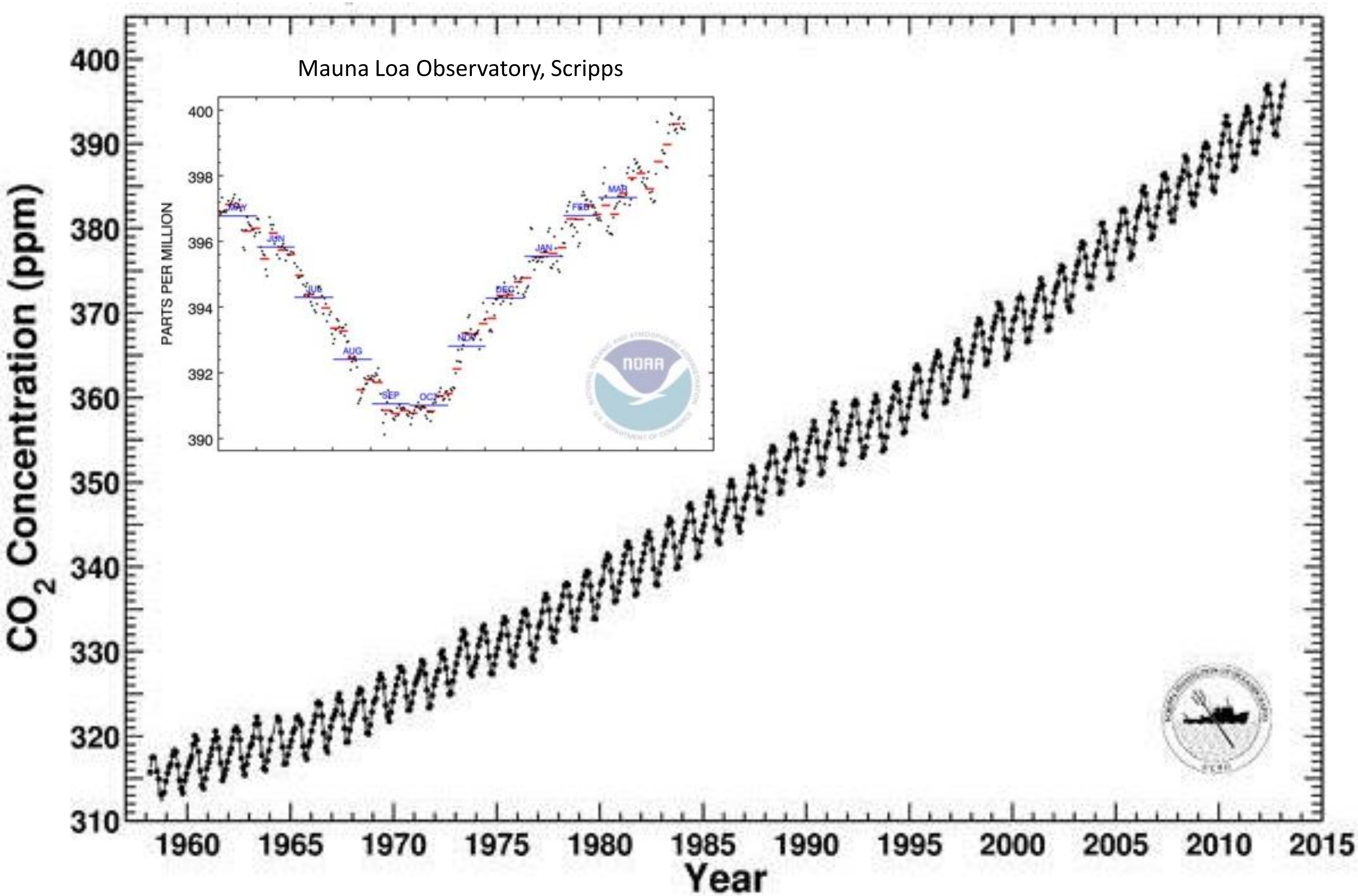
Carbon Dioxide Concentrations are Increasing...



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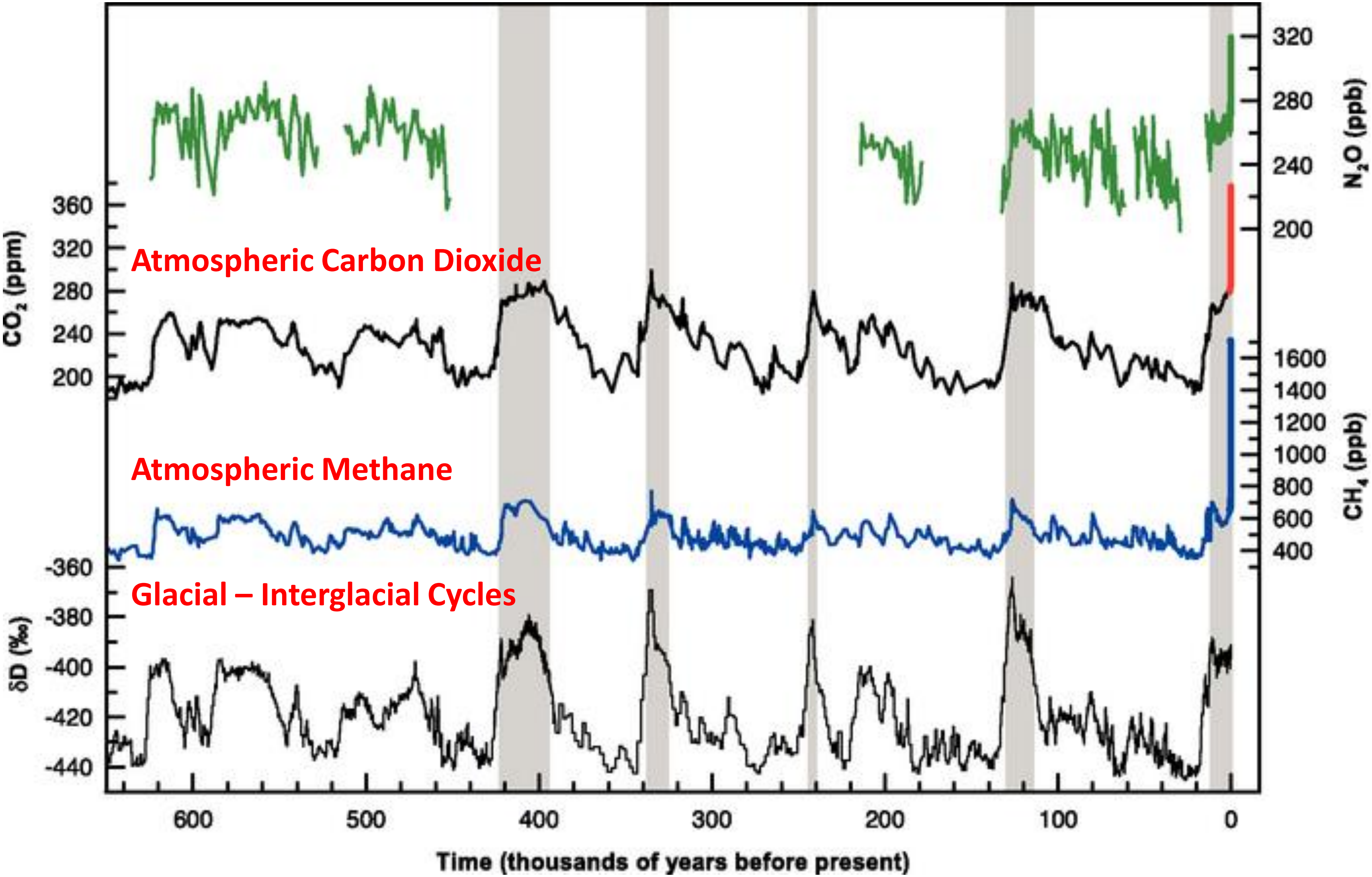

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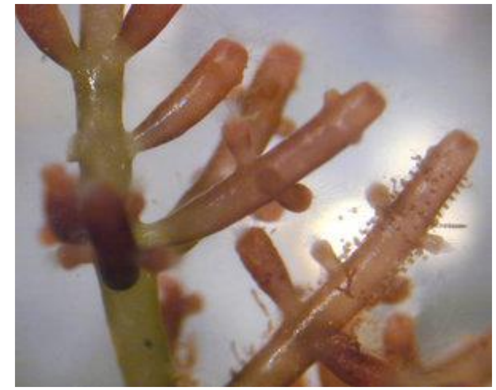
Quick Overview of the Carbon Cycle

Carbon in the ocean-atmosphere system

Organic carbon

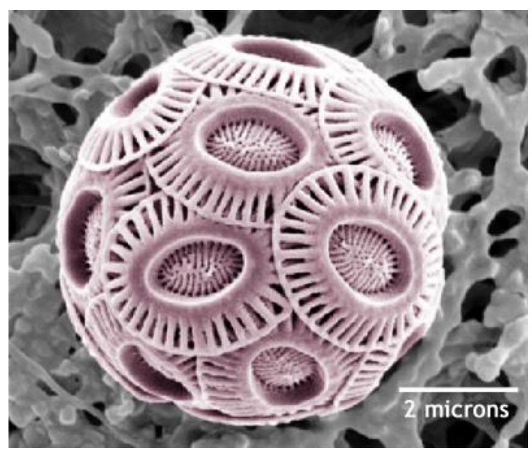
Biological carbon



Inorganic carbon

Dissolved species: CO_2, CO_3^{2-}

But also calcium carbonate (limestone)



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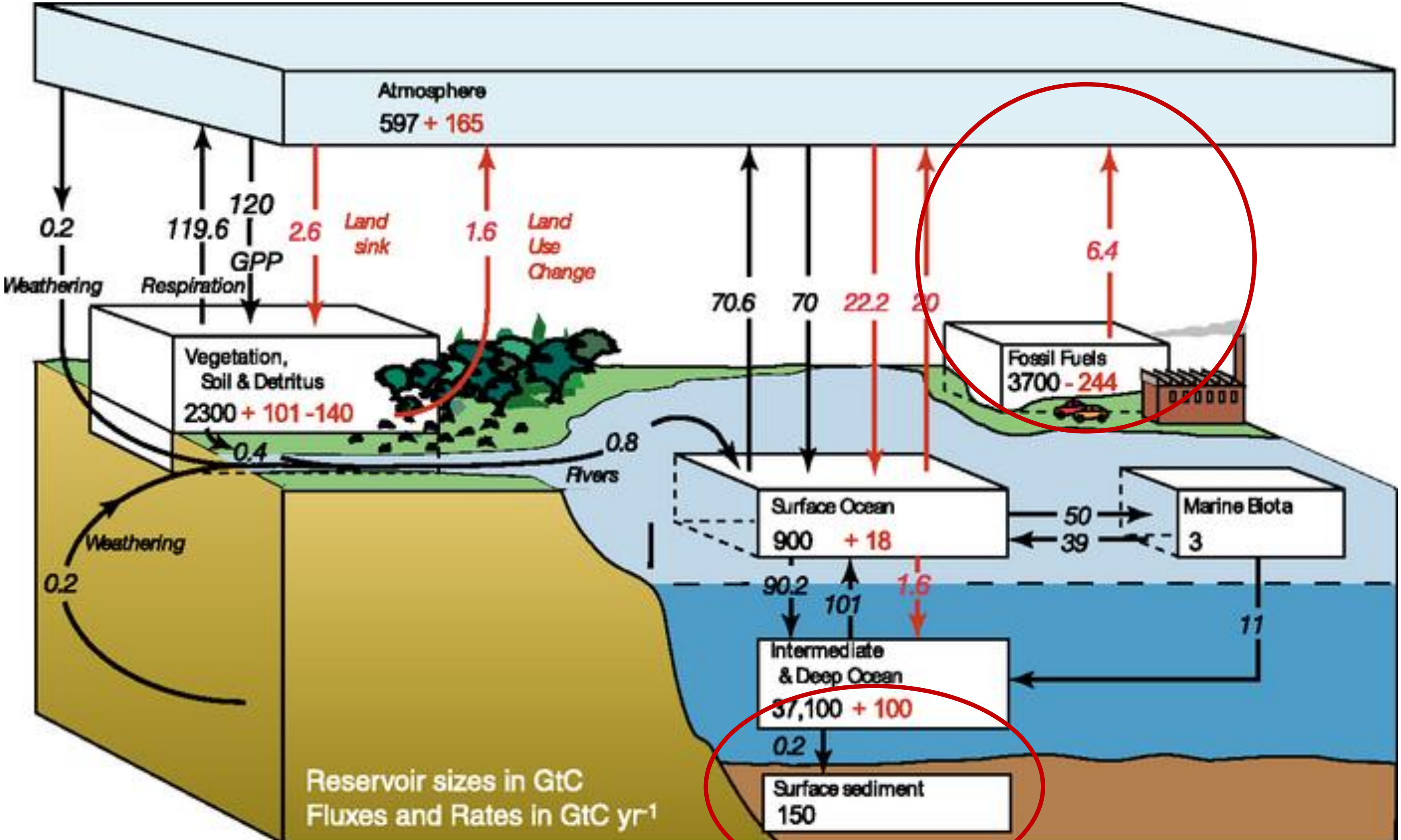
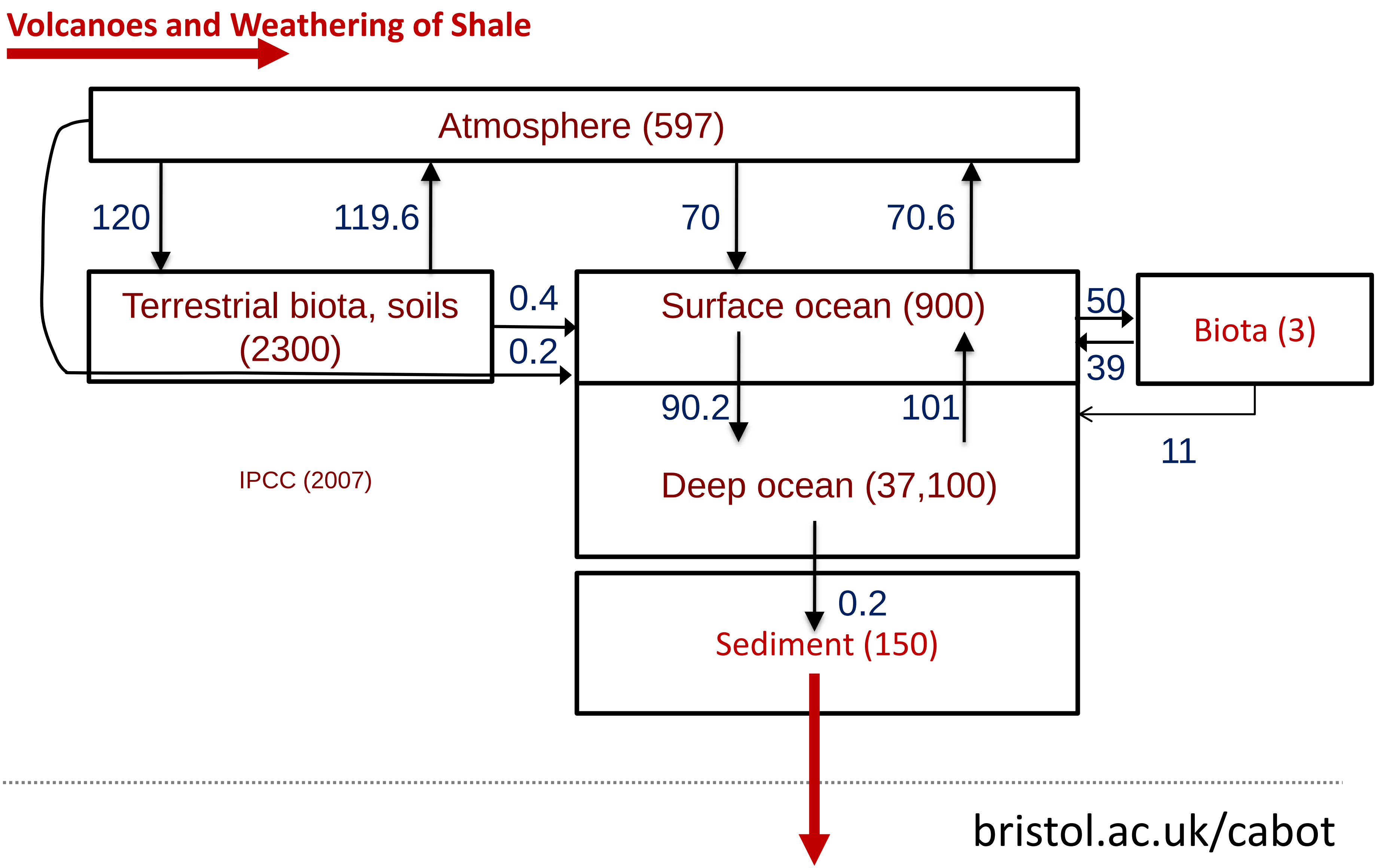


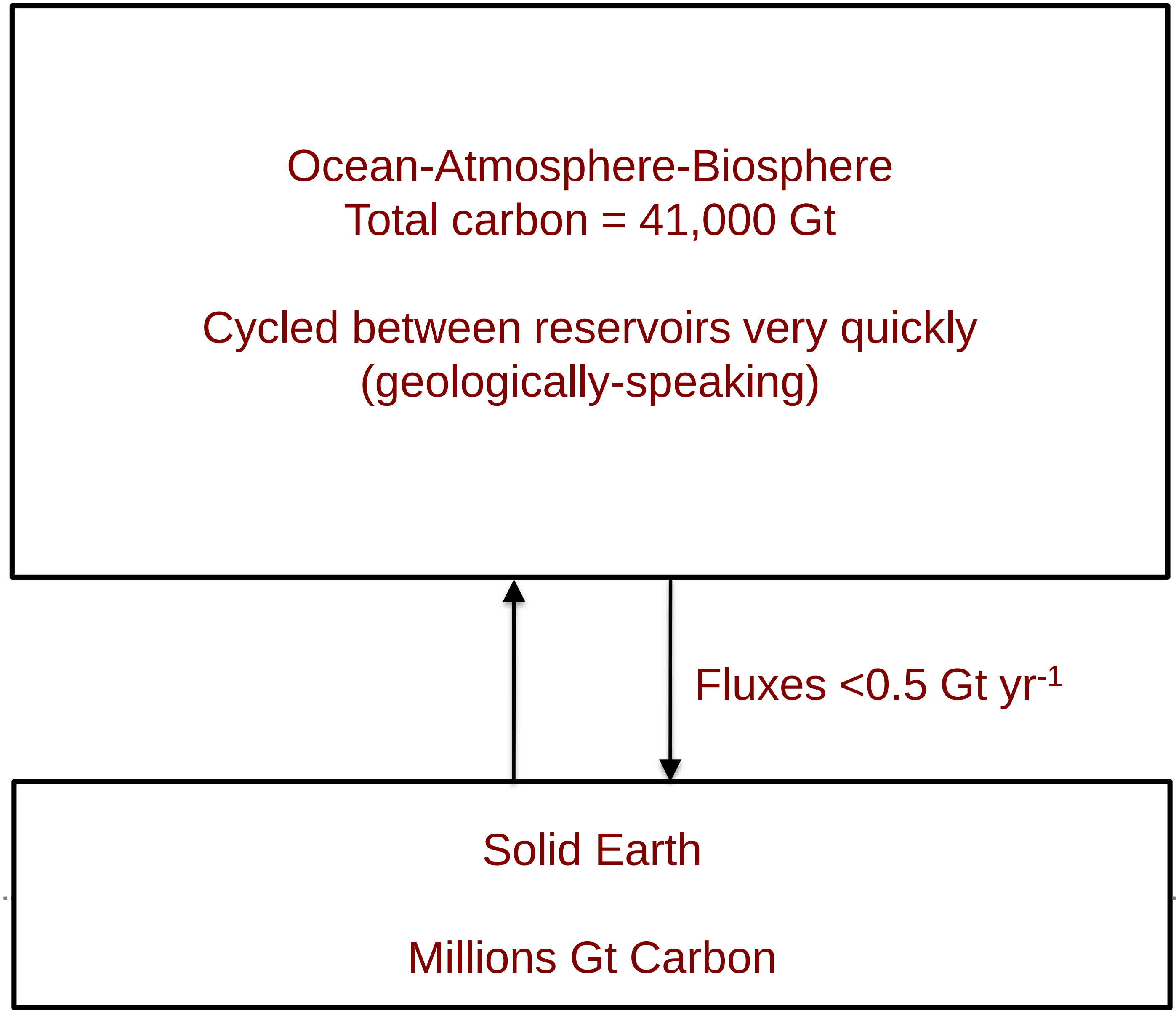
Reservoir sizes in Gt C (*not* Gt CO_2) = petagram (Pg) = 1×10^{15}g
Fluxes in Gt C yr^{-1}

The natural "short"-term carbon cycle



IPCC (2007)

The natural “long”-term carbon cycle



Many of our interests and challenges are about the long-term carbon cycle or about perturbations to it.

So why are we going to talk about the short-term carbon cycle?

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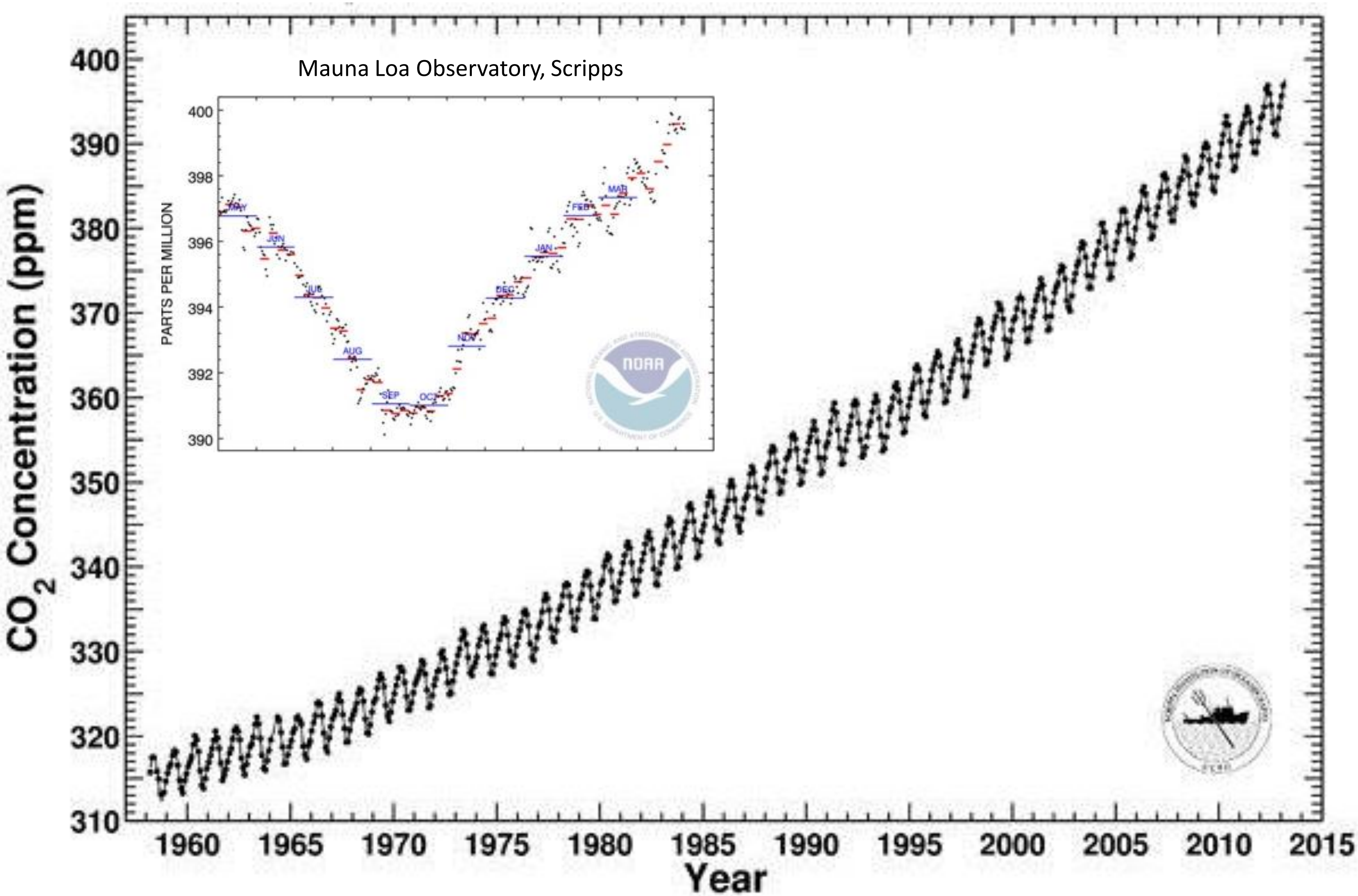
Organic Carbon is largely about photosynthesis and respiration

(i.e. oxygen and light)

Carbon Dioxide Concentrations are Increasing...



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Redox Chemistry

Life needs two things:

Energy

A way to reduce CO_2 to form biomass – Redox potential

Reflects the flow of electrons from one atom or molecule to another

Thus can be considered as two reactions

Oxidation and Reduction

This can *generate energy* (ΔG) or electrical potential (Eh)

ΔG^o (Gibbs free energy)

By convention negative values indicate that products are favoured in equilibrium

Energy is available if a solution is not in equilibrium

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Thermodynamics

What is the equilibrium distribution of compounds?

$$\Delta G^o = -RT \ln K, \quad \text{where } K = \frac{\gamma C^c \times \gamma D^d}{\gamma A^a \times \gamma B^b}$$

$$\text{where } K \sim \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

for

$$aA + bB \rightleftharpoons cC + dD$$

Thermodynamic energy is available when compounds are *not in equilibrium*

$$\Delta G = -RT \ln \frac{K}{Q} = \Delta G^o + RT \ln Q$$

Kinetics

$$\text{Rate} = k[A][B]$$

k is defined by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Where: A = Maximum rate of reaction

E_a = Activation energy

Activation Energy: For any reaction to occur, there must be collisions between species; however at close distances, most species show mutual repulsion. This acts as an energy barrier to the reaction that must be overcome.

Photosynthesis

Primary production by photosynthesis:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ + \text{trace metals (Fe, Zn, Cu, Cd, Co)} \underset{\text{Light}}{\rightleftharpoons} C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

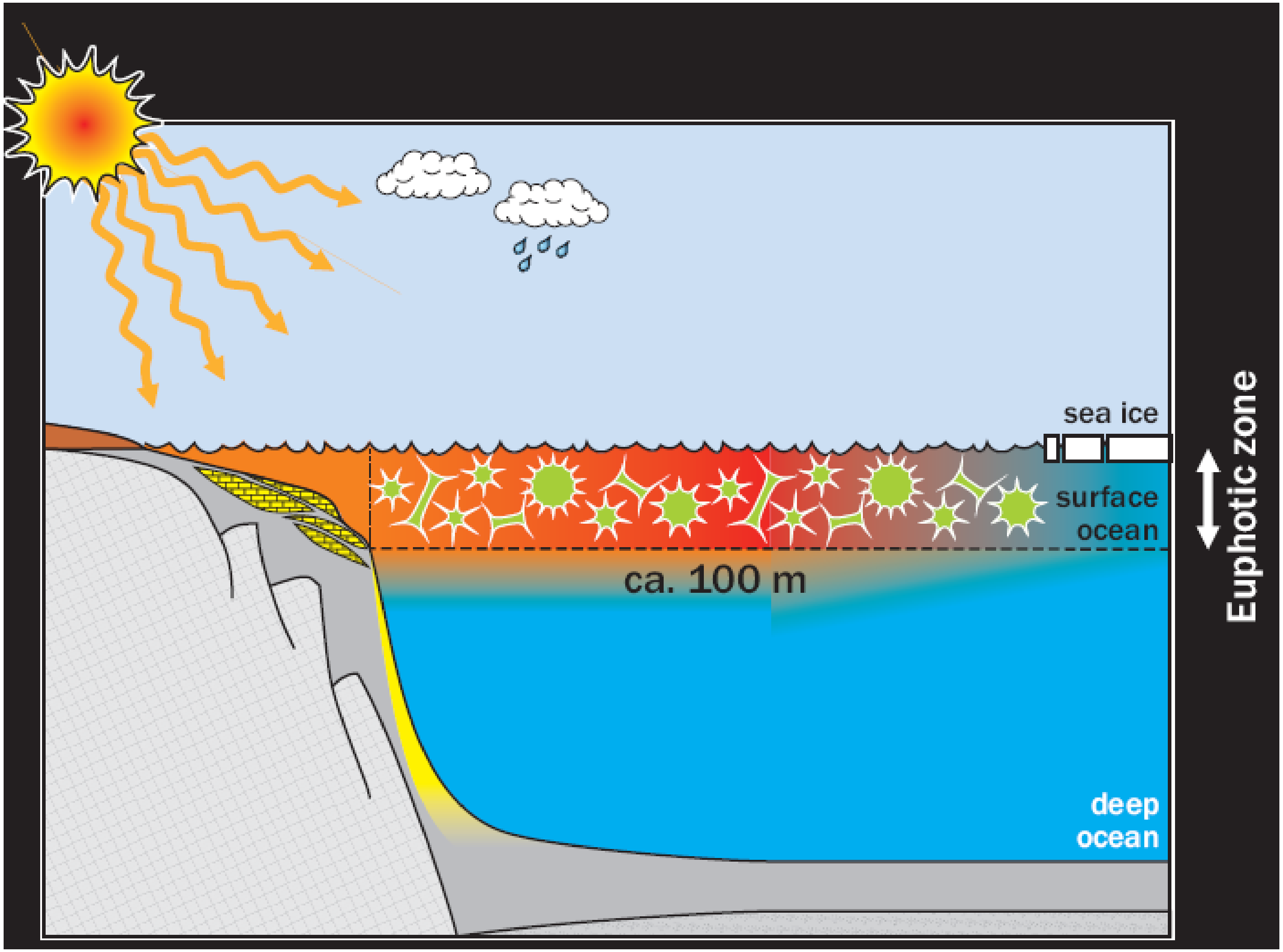
In terms of Redox:

$$\mathbf{CO_2 + H_2O \rightleftharpoons CH_2O + O_2}$$
$$\mathbf{HNO_3 + H_2O \rightleftharpoons NH_3 + 2\,O_2}$$

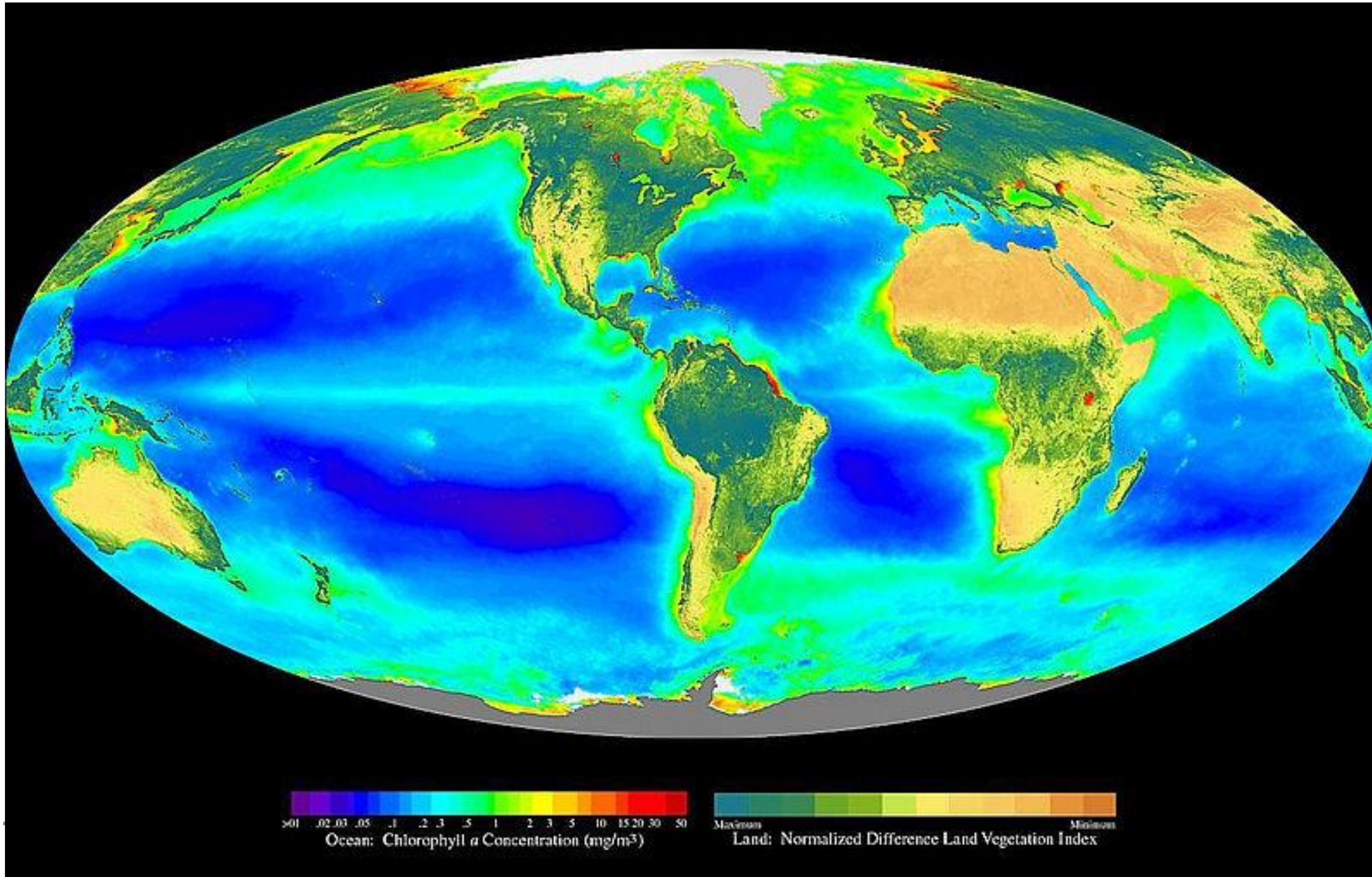
In terms of Chemical Compounds, roughly:

CH_2O = Carbohydrate
NH_3 = Amine (Amino Acid = Protein)
PO_4 = DNA, RNA, Membrane lipids

What governs Photosynthesis?



What governs Photosynthesis?



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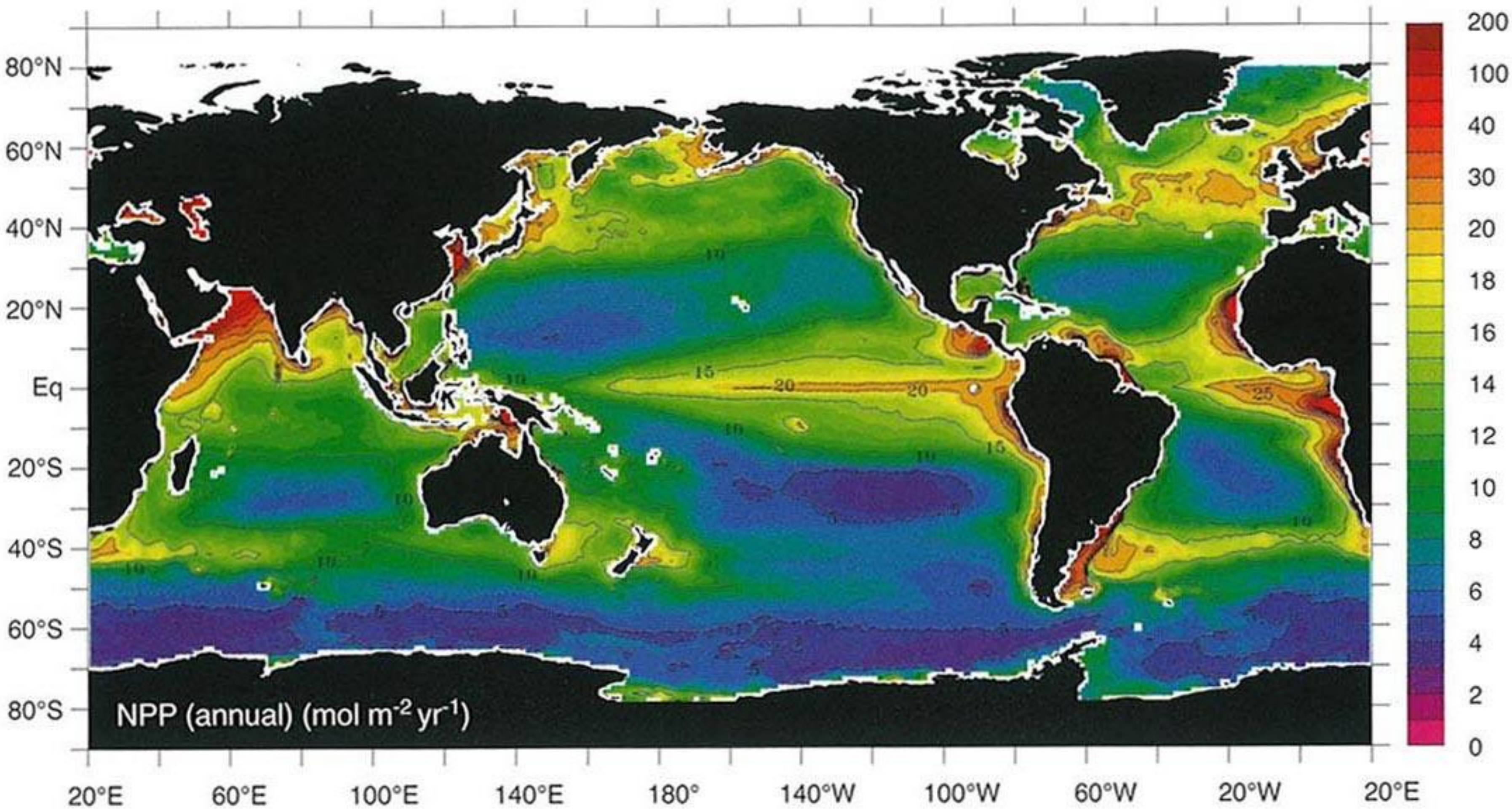
What governs Photosynthesis?



From: Sarmiento and Gruber (2006) Ocean Biogeochemical Dynamics, Princeton University Press

Respiration

Heterotroph: organism that cannot synthesise all the organic molecules it needs using only inorganic compounds; instead they oxidise organic carbon to carbon dioxide to yield cellular energy **(respiration)**

$$CH_2O + O_2 \rightleftharpoons CO_2 + H_2O$$

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightleftharpoons 106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4$$

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What controls Respiration?

ΔG°

Aerobic Respiration

$$\text{'}CH_2O\text{'} + O_2 \rightleftharpoons CO_2 + H_2O \qquad -29.9$$

Denitrification

$$5\text{'}CH_2O\text{'} + 4NO_3^- + 4H^+ \rightleftharpoons 5CO_2 + 2N_2 + 7H_2O \qquad -28.4$$

Sulfate Reduction

$$2\text{'}CH_2O\text{'} + SO_4^{2-} + \rightleftharpoons 2HCO_3^- + H_2S \qquad -6.1$$

Methanogenesis

$$2\text{'}CH_2O\text{'} \rightleftharpoons CO_2 + CH_4 \qquad -5.6$$

Hydrogen Fermentation

$$\text{'}CH_2O\text{'} + H_2O \rightleftharpoons CO_2 + 2H_2 \qquad -1.6$$

Two take-home messages: Lots of oxidants (but O_2 is the best)
Strong interactions between carbon and other element cycles

What controls Respiration?

$$\text{Rate} = k[A][B]$$

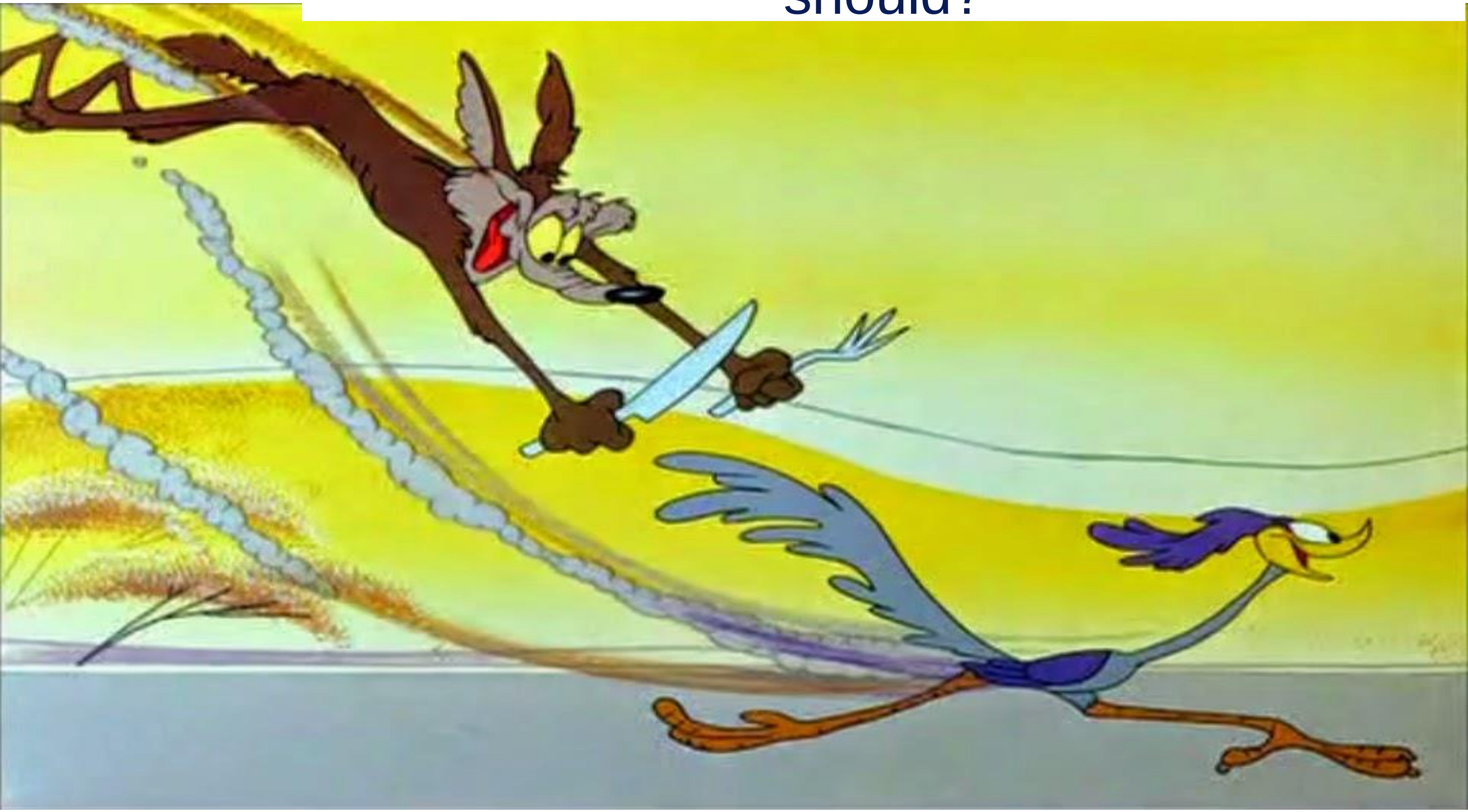
k is defined by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Where: A = Maximum rate of reaction
E_a = Activation energy

Activation Energy: For any reaction to occur, there must be collisions between species; however at close distances, most species show mutual repulsion. This acts as an energy barrier to the reaction that must be overcome.

But why doesn't everything degrade….. eventually? As thermodynamics says it should?



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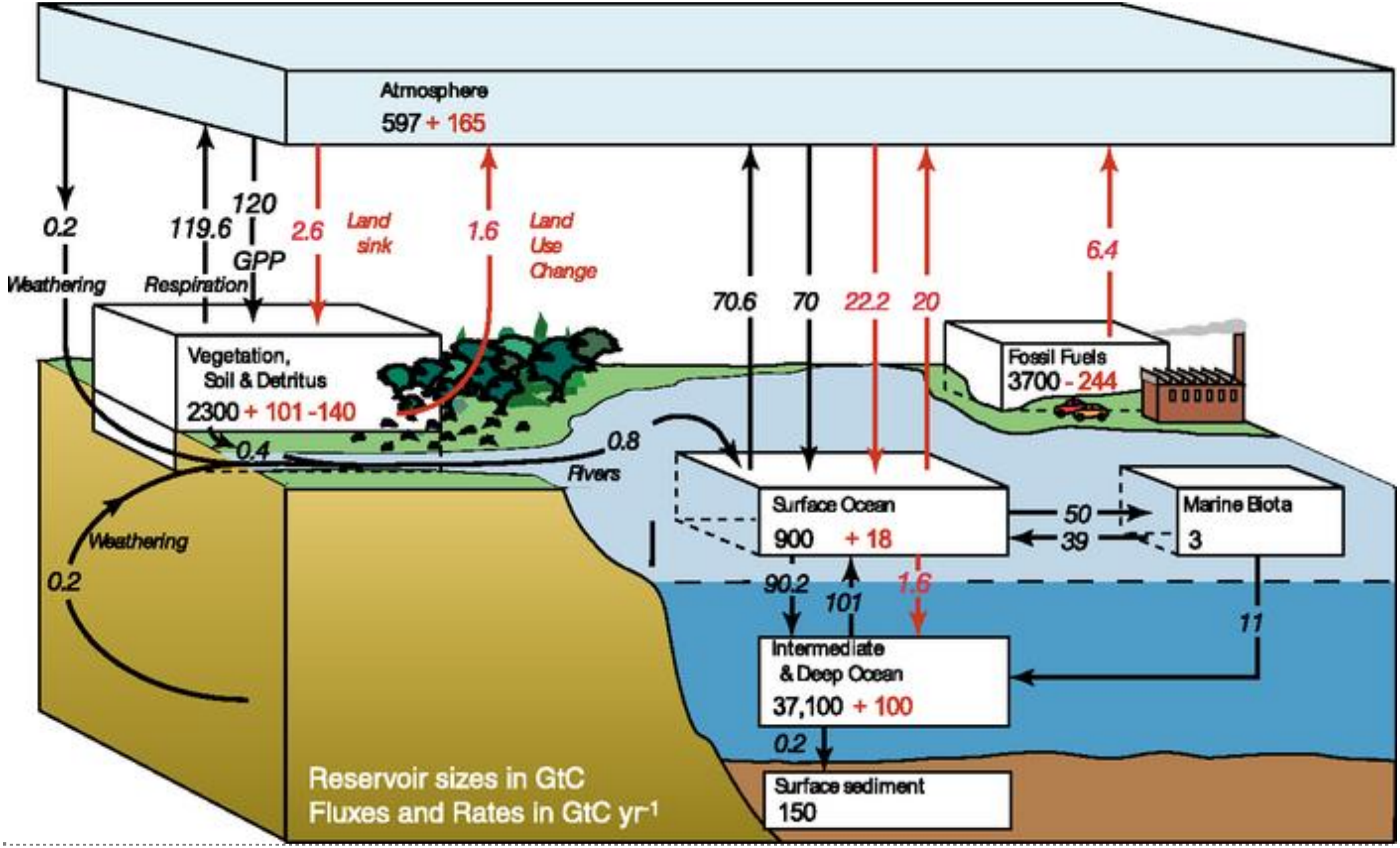

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Fluxes in Gt C yr^{-1}

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The inorganic carbon cycle is basically about pH

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When CO_2 dissolves in water, it is an acid

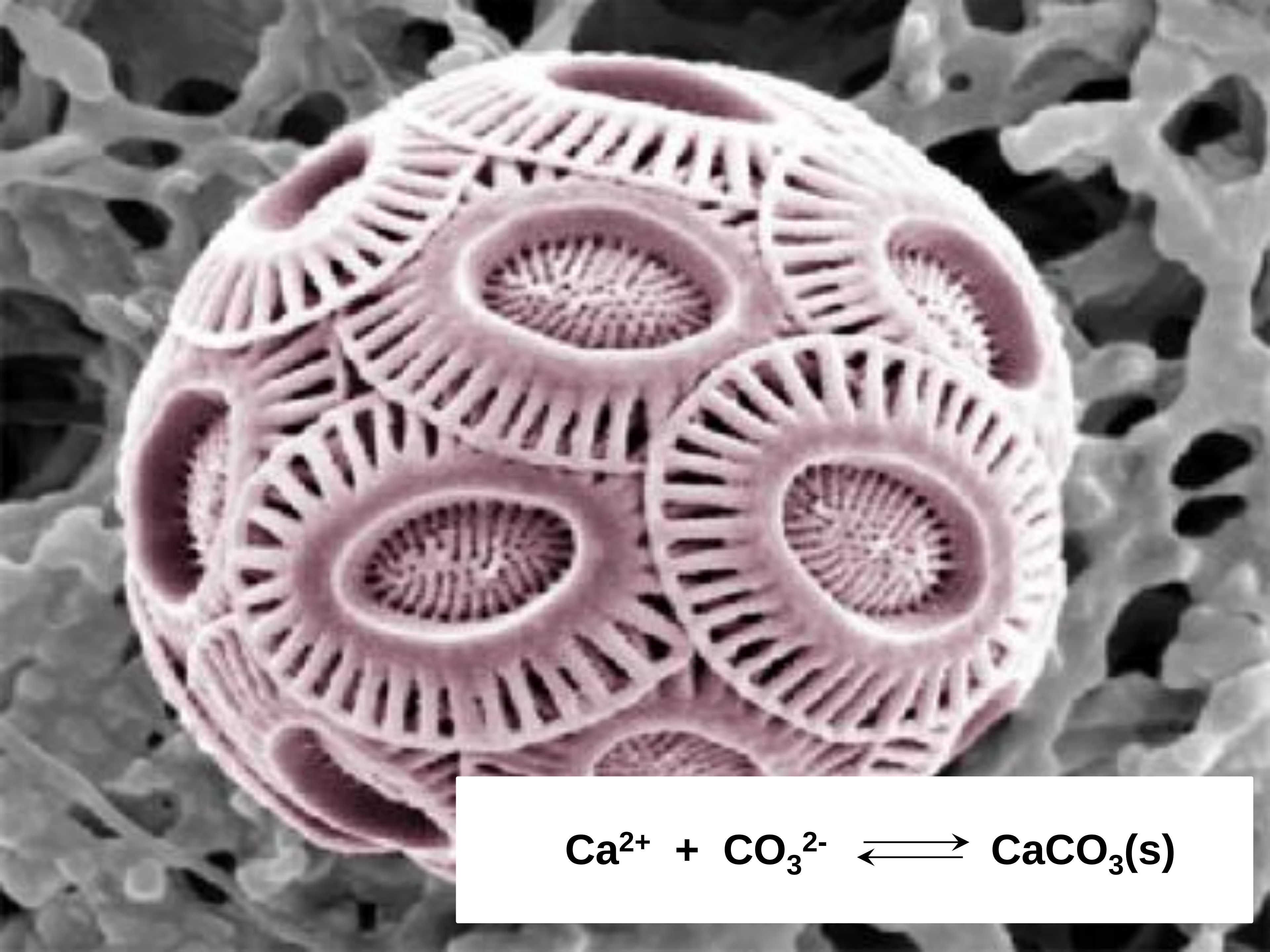
Dissolved Inorganic Carbon occurs as several dissolved *species*

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$$

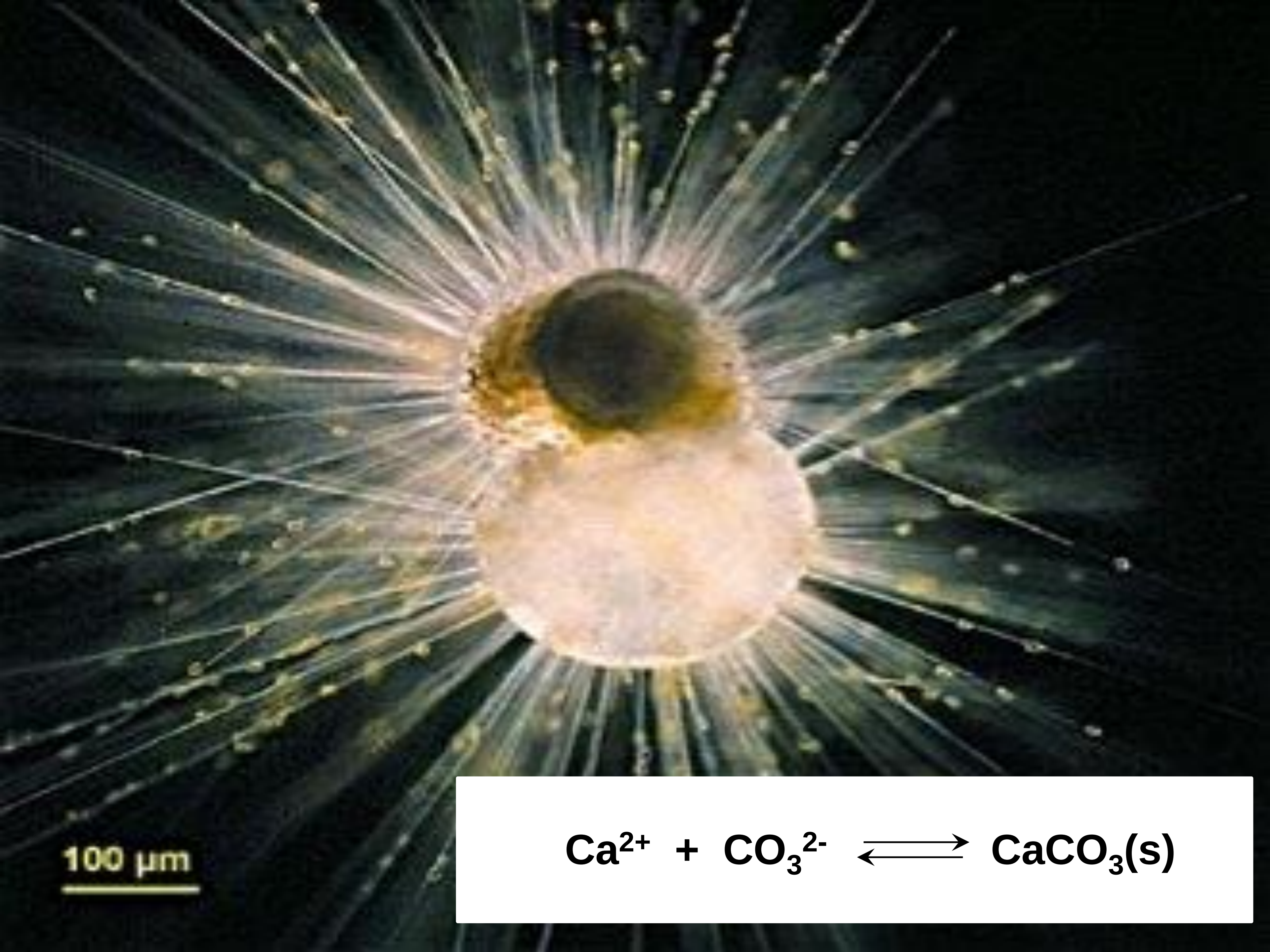
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$\Sigma CO_2 = \text{Total DIC} = CO_2(aq) + H_2CO_3 + HCO_3^- + CO_3^{2-}$$



$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(s)$$



$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(s)$$

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$$CO_{2(aq)} + CaCO_3(s) + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

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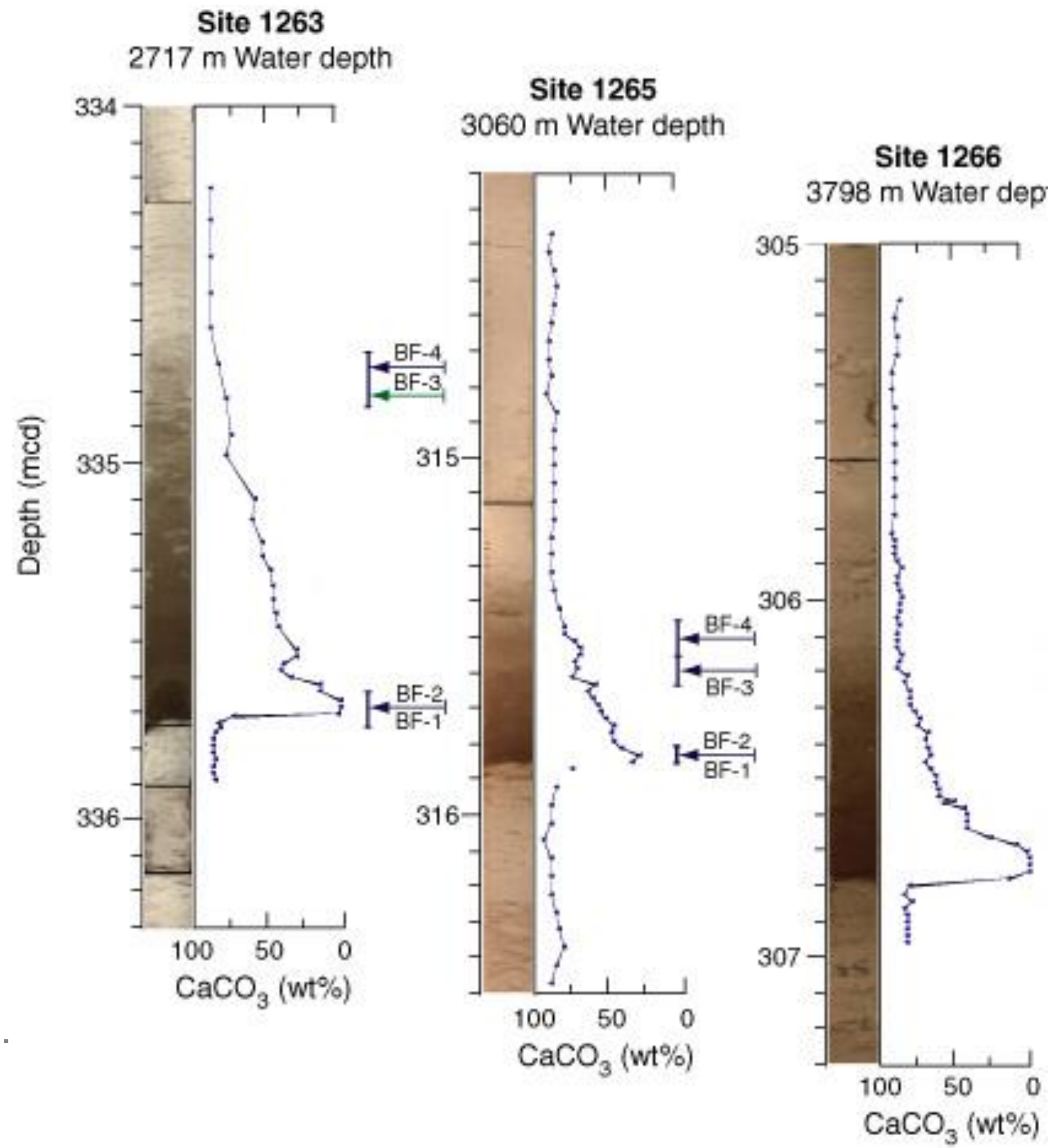
$$CO_{2(aq)} + CaCO_3(s) + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$



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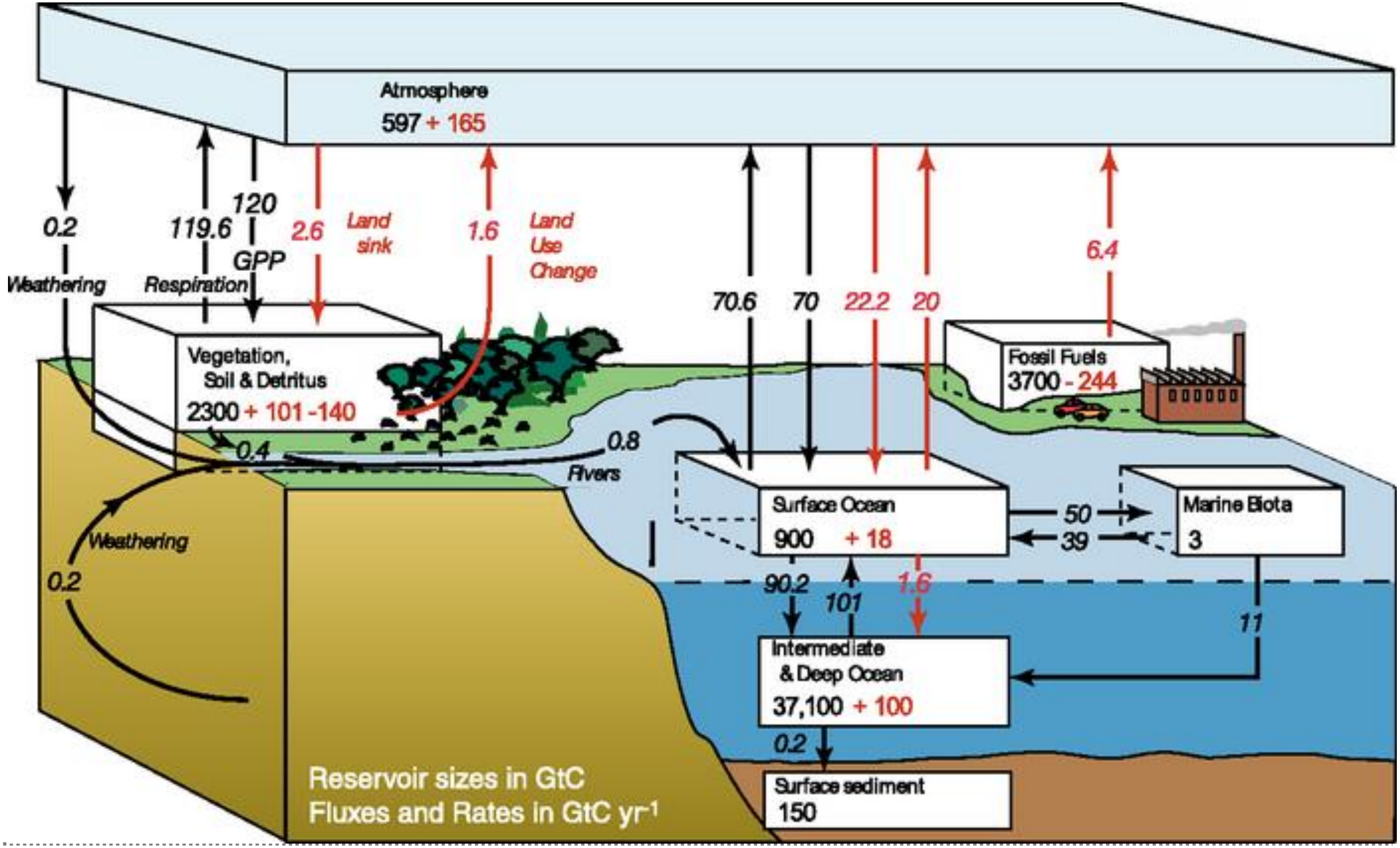

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So what is the global carbon cycle about?

Life!!

Life's origin and its evolution

Photosynthesis and Respiration

The history of carbon dioxide and of methane

The formation of oil and coal

The industrial age, fossil fuels and global warming

The deep biosphere and exotic organisms

The fate of permafrost and soil

The things that vary with carbon redox reactions – nutrients in the ocean to toxic metal contamination