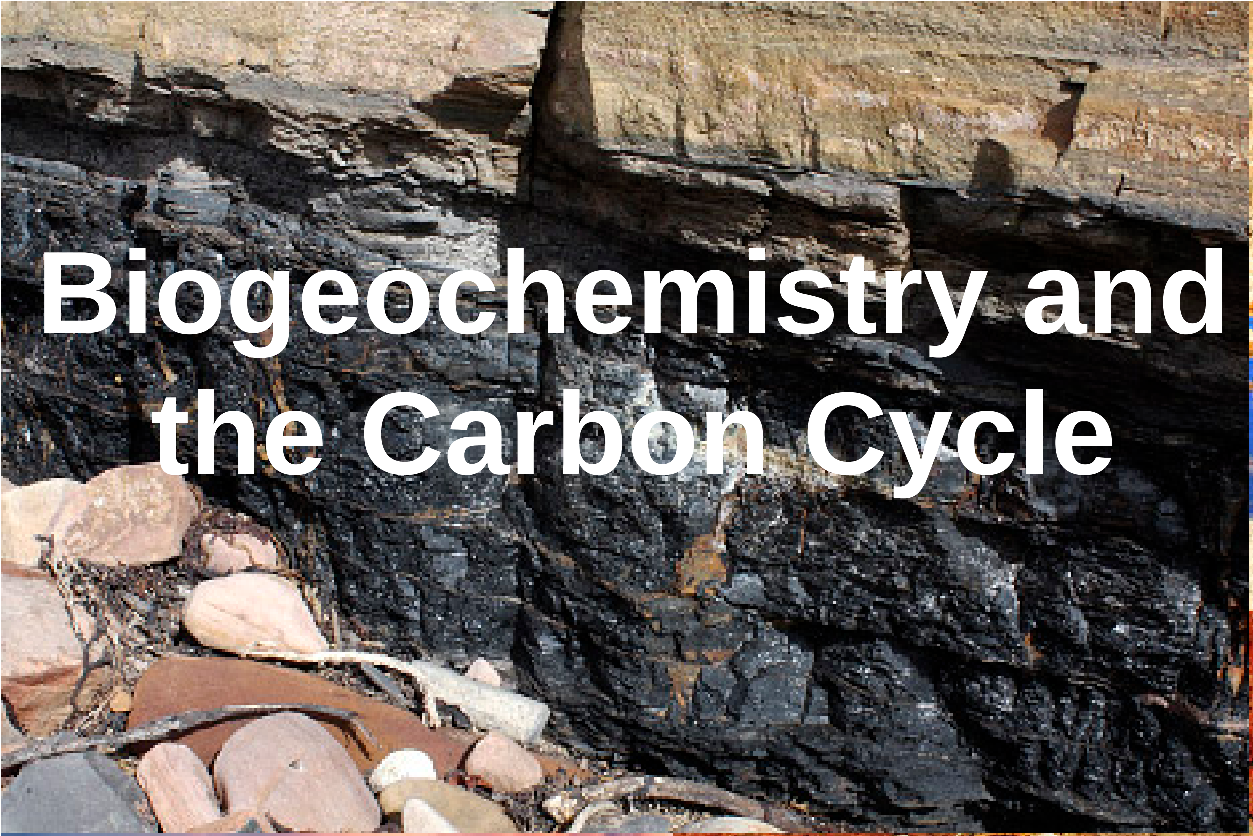
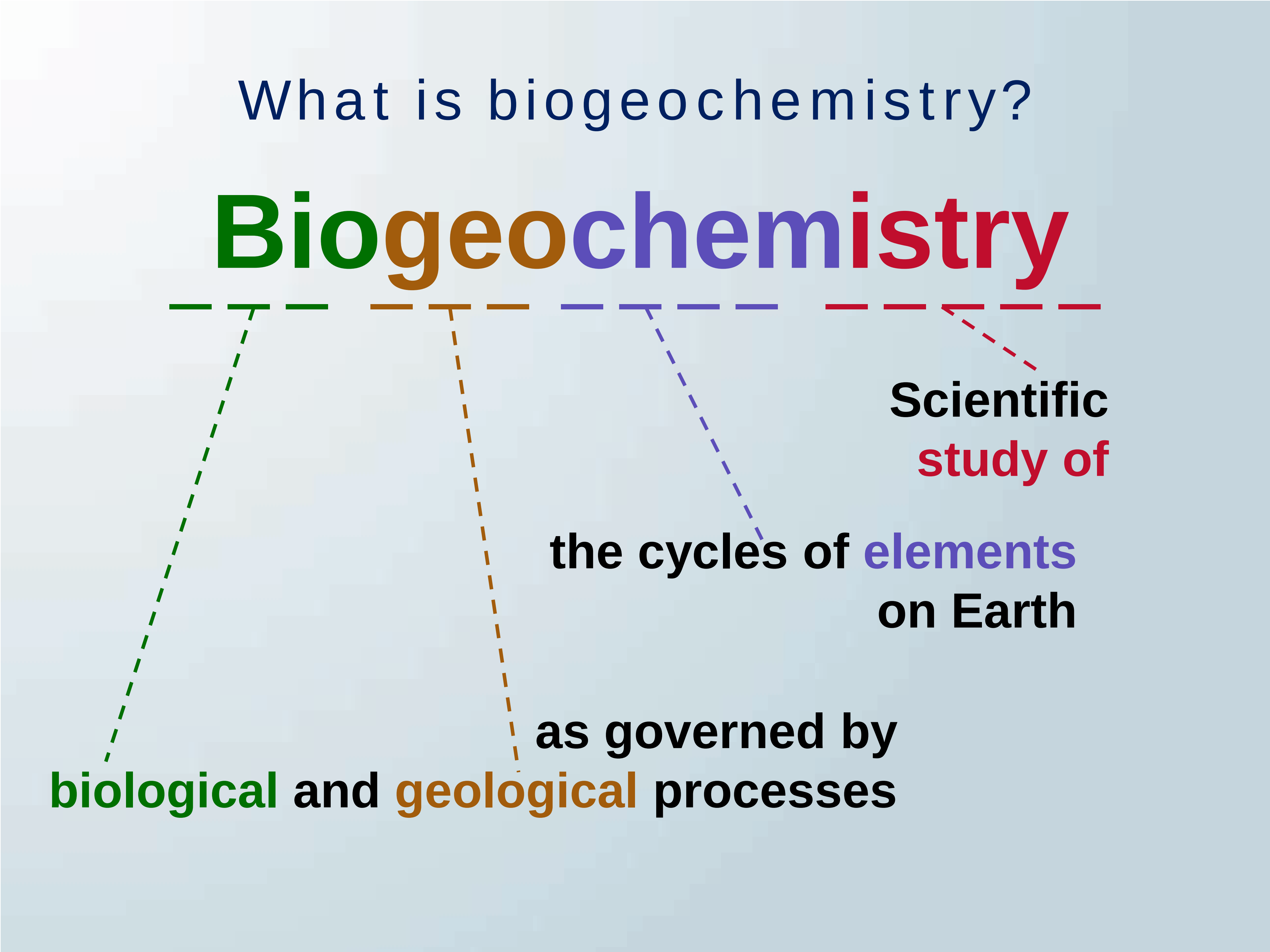
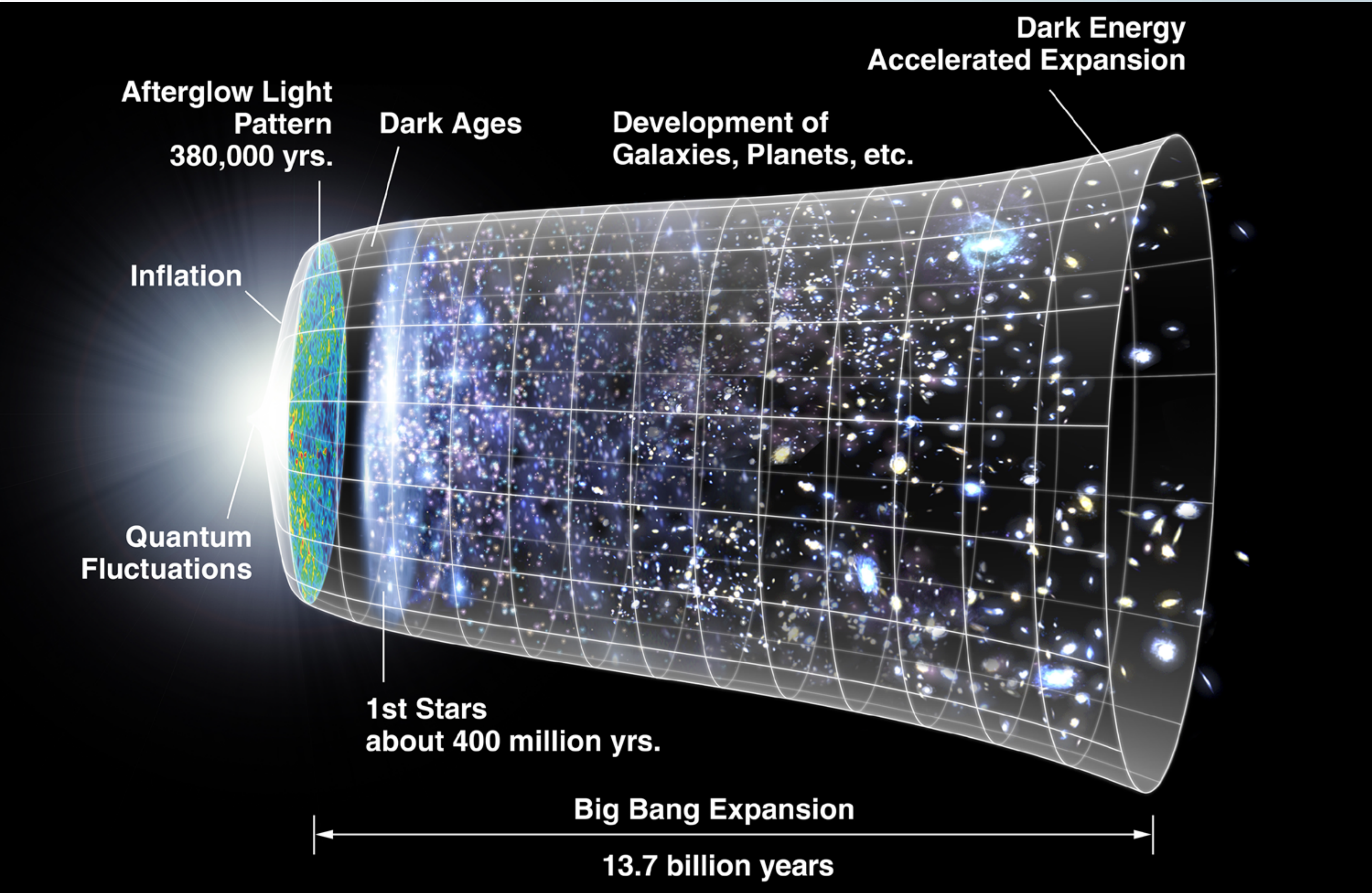
Biogeochemistry and the Carbon Cycle



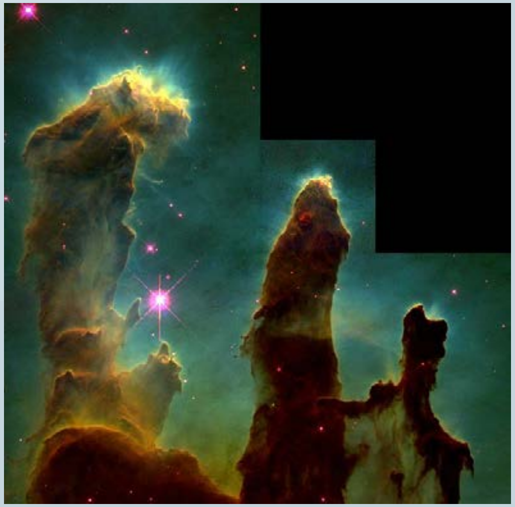

What is biogeochemistry?
Biogeochemistry
Scientific
study of
the cycles of elements
on Earth
as governed by
biological and geological processes

It started with the Big Bang…



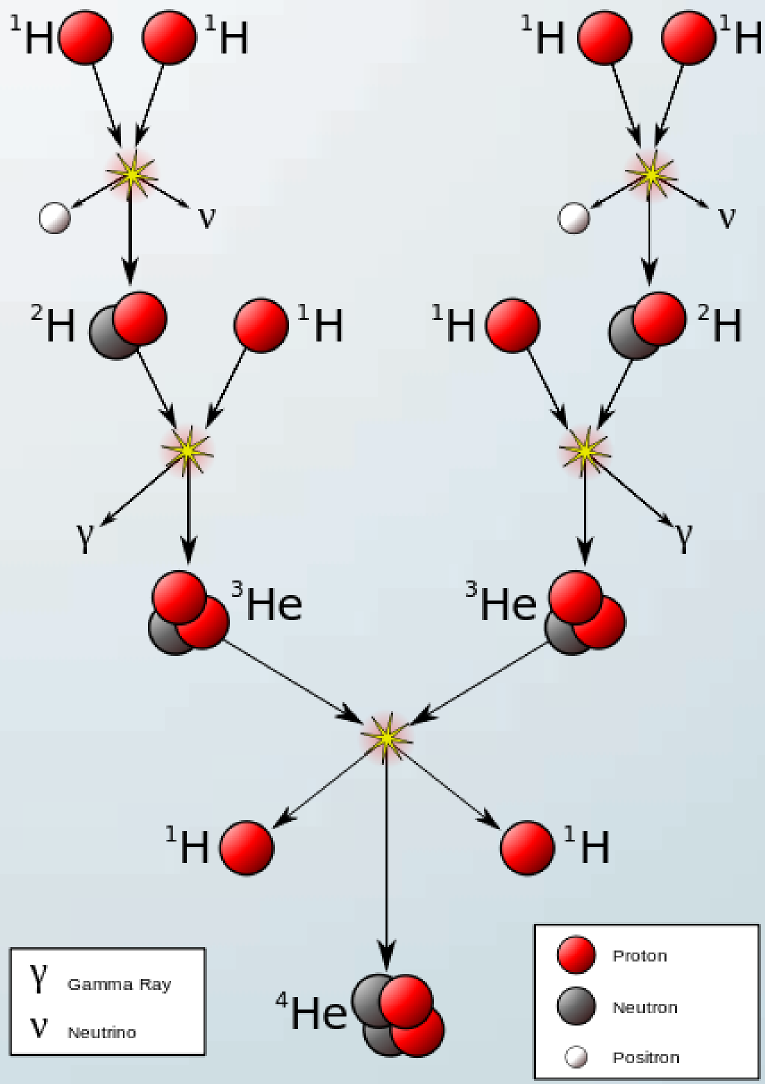
Brief History of the Elements

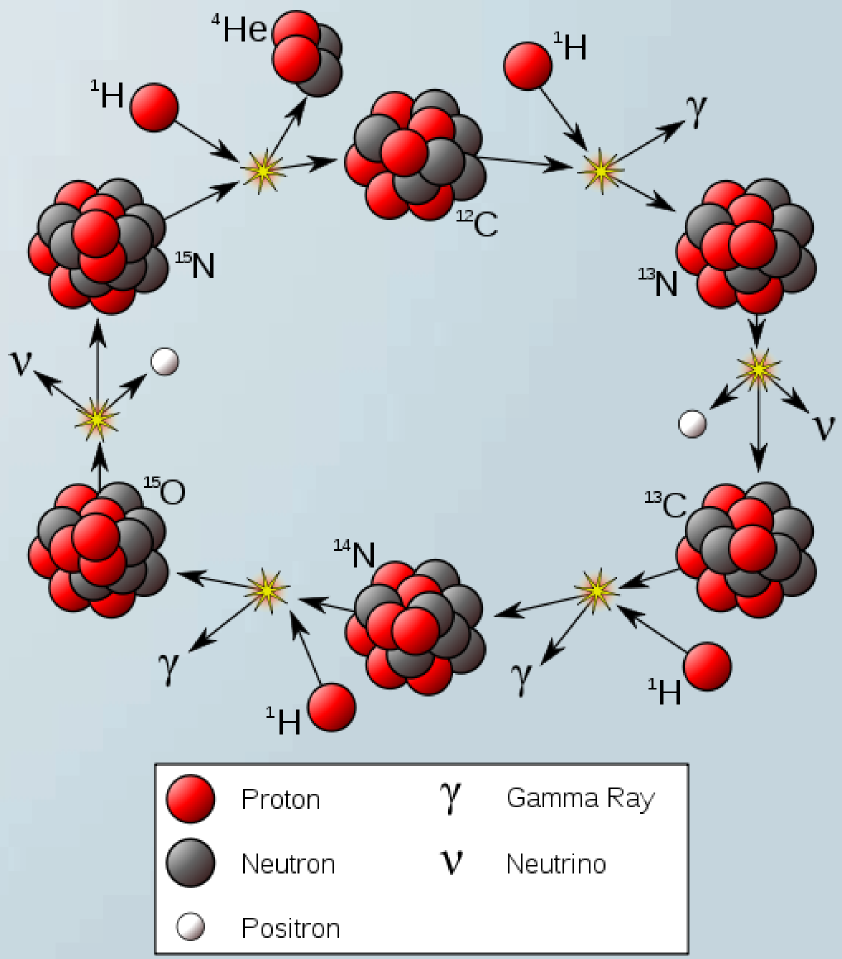
- **Big Bang Nucleosynthesis**, 3-20 minutes after space expansion – formed deuterium (H-2), the helium isotopes He-3 and He-4, and the lithium isotopes Li-6 and Li-7. Also formed unstable isotopes tritium (H-3) and beryllium-7 (Be-7), and beryllium-8 (Be-8). These unstable isotopes either decayed or fused with other nuclei to make one of the stable isotopes. After 20 minutes, density too low to continue.
- Dense regions within molecular clouds in space collapse into spheres of plasma to form stars.



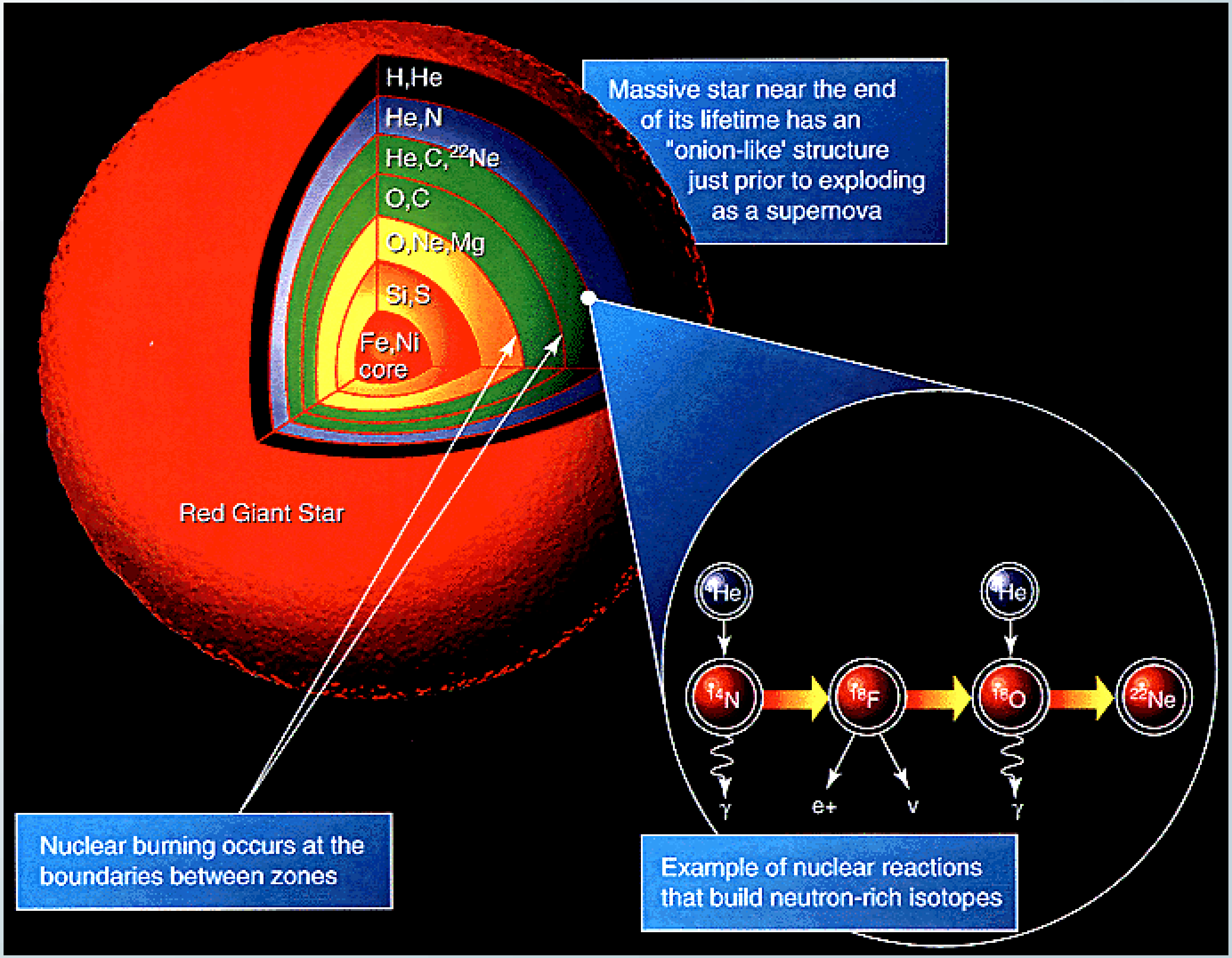
Hubble telescope image known as *Pillars of Creation,* where stars are forming in the Eagle Nebula.

A Brief History of Earth's Elements – Stellar Nucleosynthesis



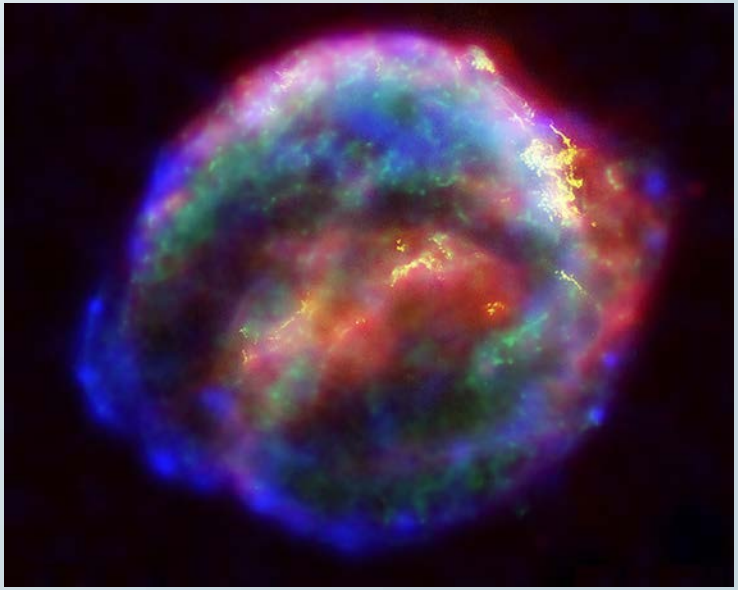


A Brief History of Earth's Elements – Stellar Nucleosynthesis



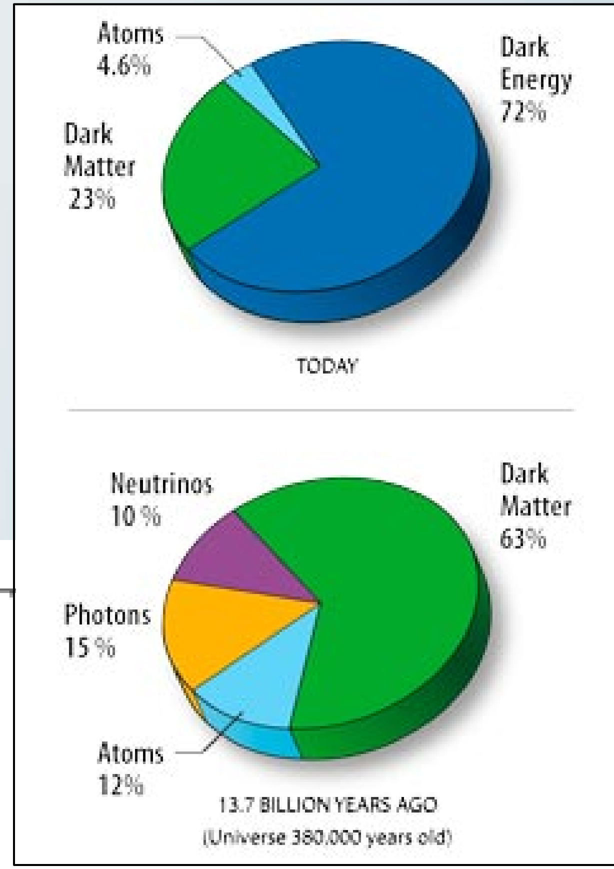
A Brief History of Earth's Elements – Supernova Nucleosynthesis

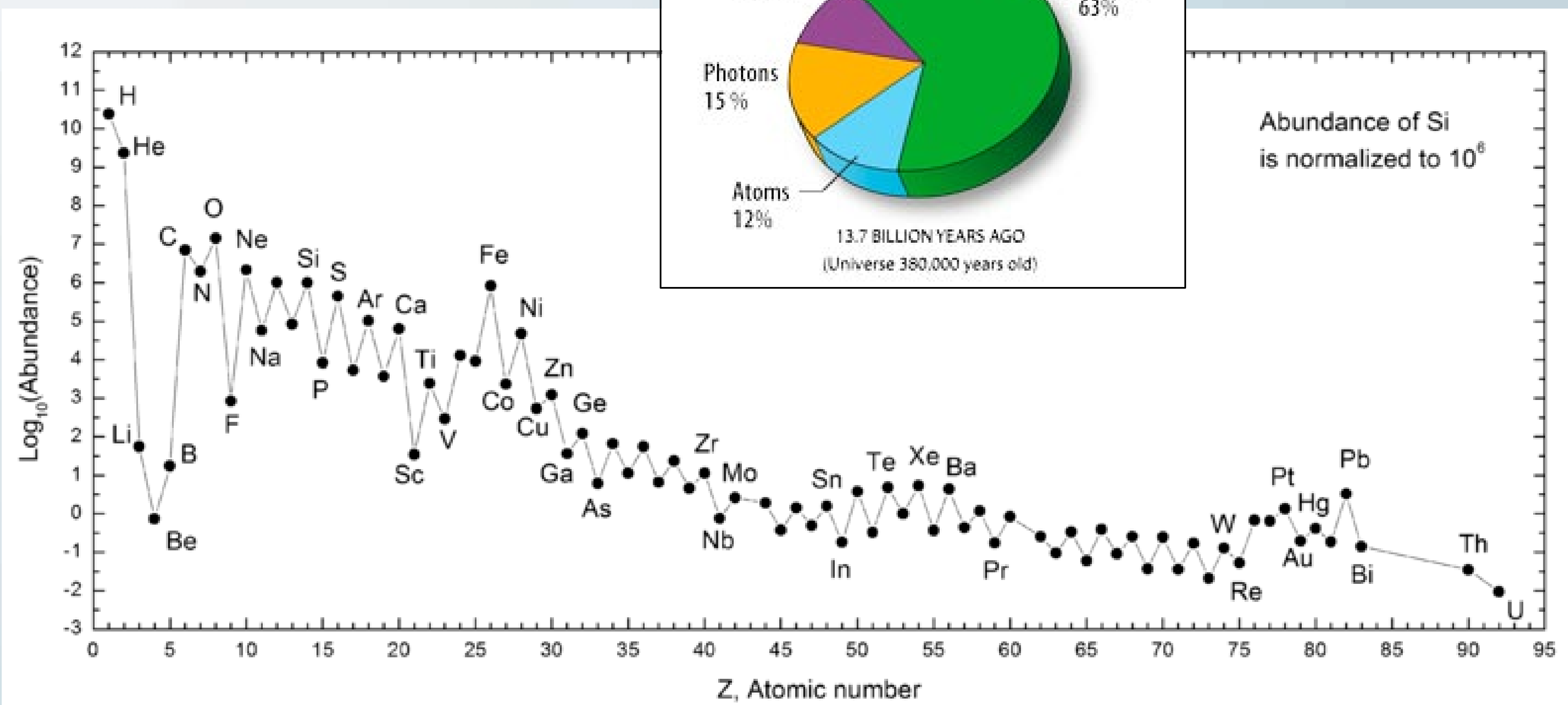
- Supernovas form heaviest elements, scatter them into space.
- Create the elements silicon, sulfur, chlorine, argon, sodium, potassium, calcium, scandium, titanium, iron elements vanadium, chromium, manganese, iron, cobalt, and nickel.



Kepler's Supernova

Elemental Abundance – Universe

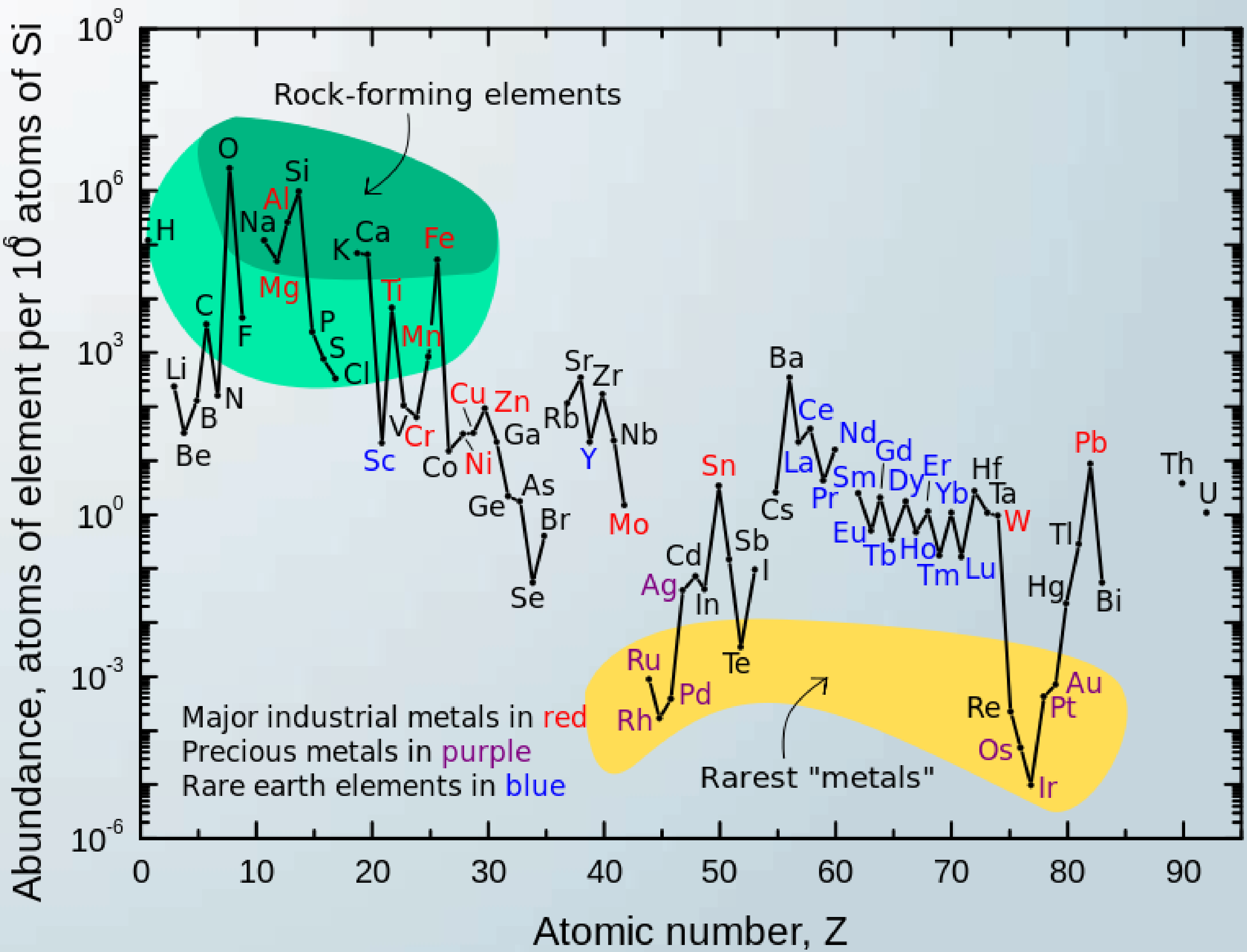




A Brief History of Earth's Elements

- Dust $\rightarrow$ planetesimals $\rightarrow$ Earth (4.5 Gy)
- Heavy elements sink to core, H & He escape
- Atmosphere forms: H_2O, CO_2, CH_4, N_2, NH_3, HCl, H_2S, SO_2
- T falls, H_2O condenses, N_2 left in atmosphere, oceans form
- Life emerges in ocean (4 Gy) $\rightarrow$ O_2 slowly builds up
- Ozone layer forms $\rightarrow$ life emerges on land (0.5 Gy)

Element Abundance Land



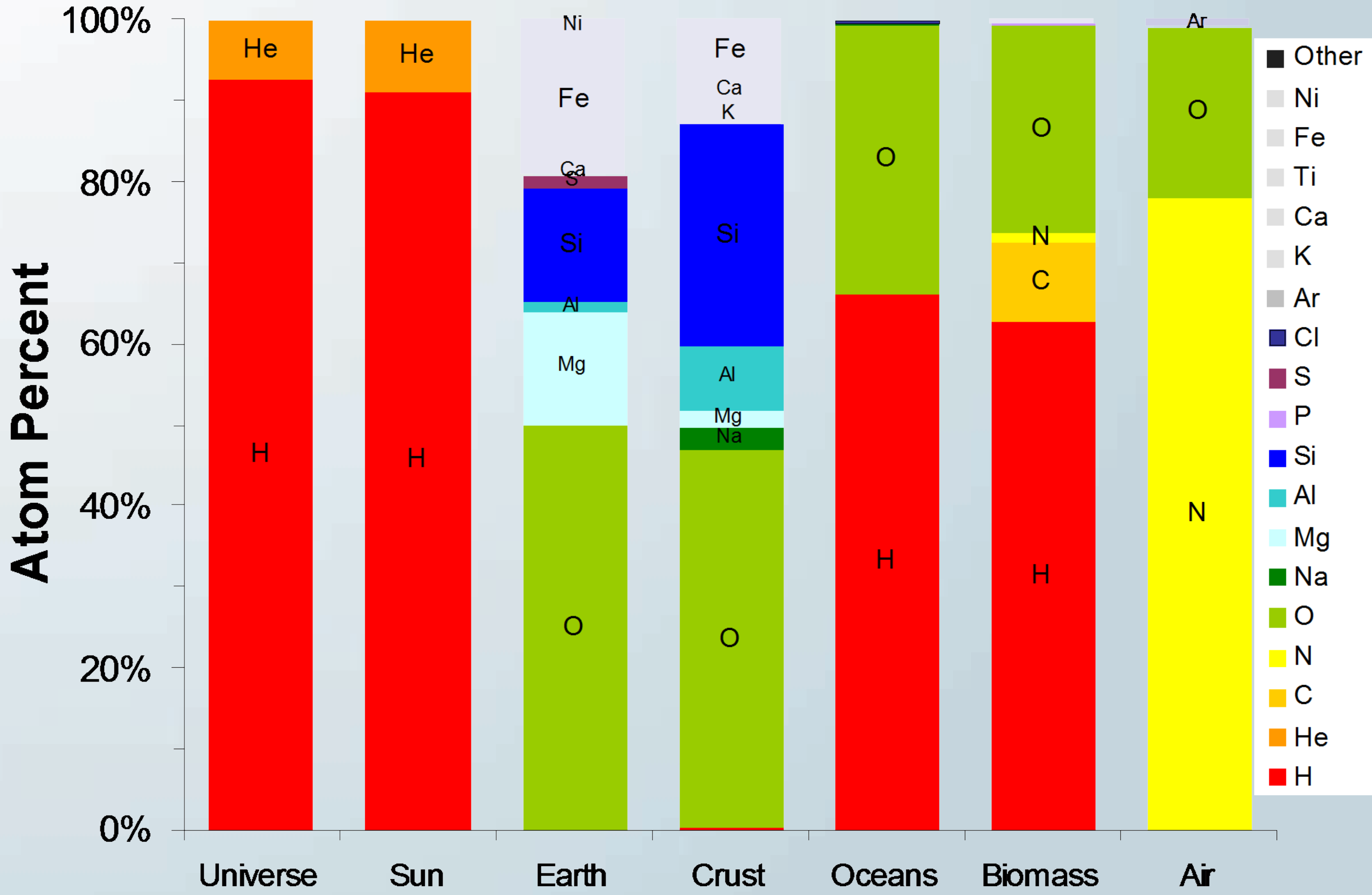
Element Abundance Oceans

Element	Proportion (by mass)
Oxygen	85.84%
Hydrogen	10.82%
Chlorine	1.94%
Sodium	1.08%
Magnesium	0.1292%
Sulfur	0.091%
Calcium	0.04%
Potassium	0.04%
Bromine	0.0067%
Carbon	0.0028%

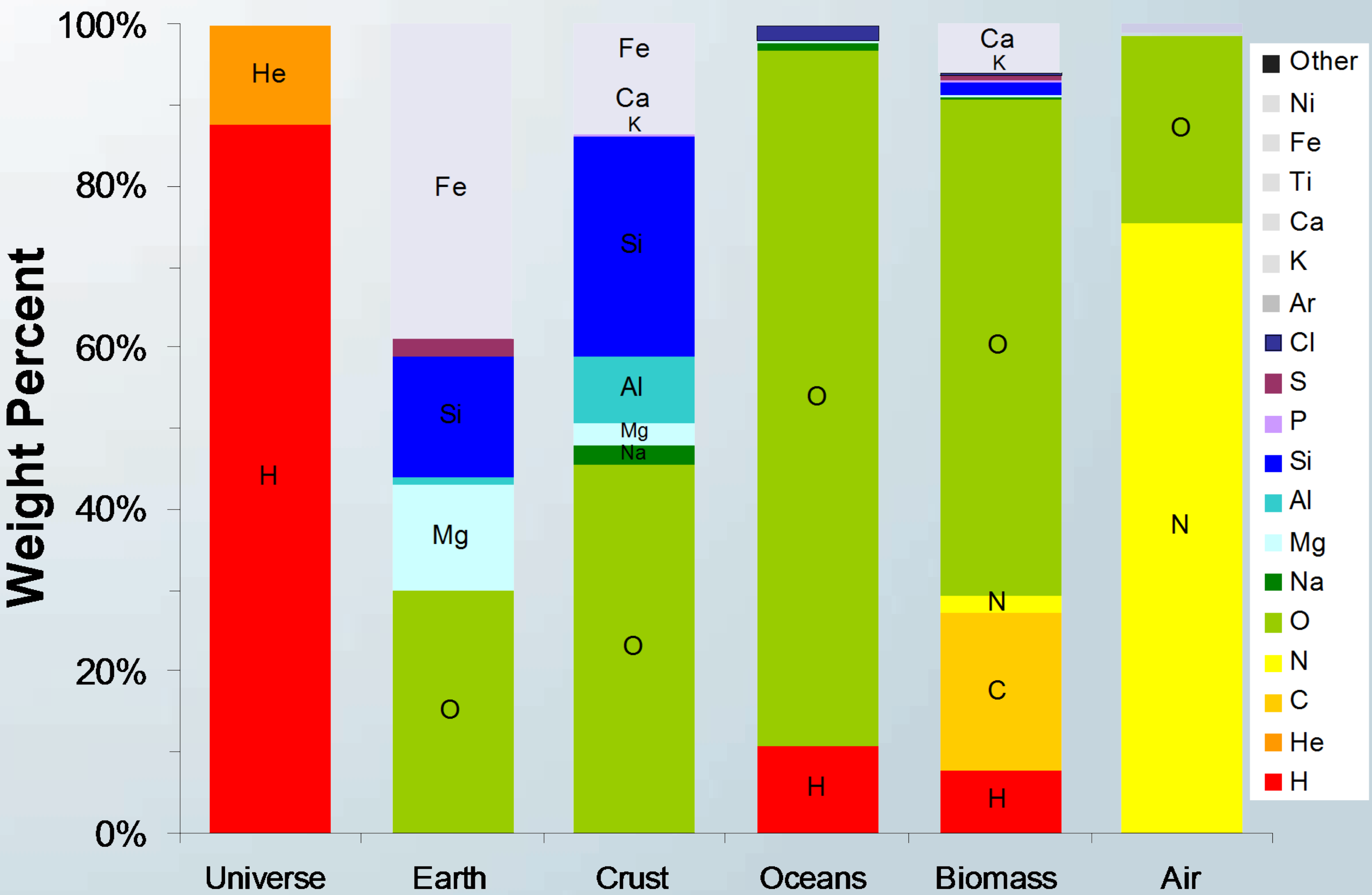
Element Abundance Humans

Element	Proportion (by mass)
Oxygen	65%
Carbon	18%
Hydrogen	10%
Nitrogen	3%
Calcium	1.5%
Phosphorus	1.2%
Potassium	0.2%
Sulfur	0.2%
Chlorine	0.2%
Sodium	0.1%
Magnesium	0.05%
Iron	< 0.05%
Cobalt	< 0.05%
Copper	< 0.05%
Zinc	< 0.05%
Iodine	< 0.05%
Selenium	< 0.01%

Elemental Abundance – Atom Percent



Elemental Abundance – Mass Percent



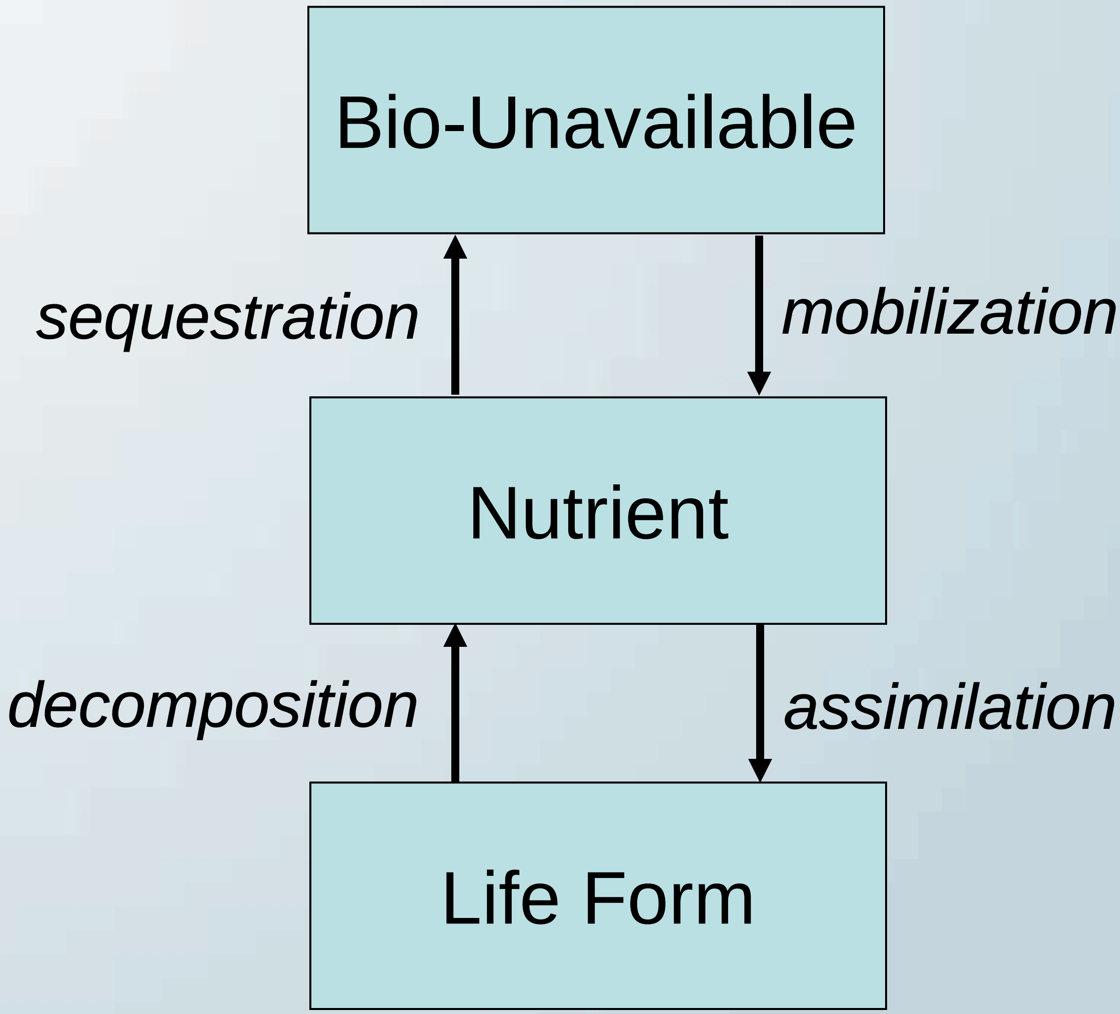
Important Chemicals for Life

- 98% of biomass is **C, H, N, O, P, S** (“CHNOPS”)
  - Average biomass: $C_{1480}H_{2960}O_{1480}N_{160}P_{18}S_{10}$
  - Hydrologic cycle (H_2O)
  - Carbon cycle (organic compounds; Ca-O compounds)
  - Nitrogen cycle (proteins, enzymes, $-NH_2$ amino acids)
  - Sulfur, Phosphorus cycles (ATP, DNA, RNA)
- These six, plus five other **macronutrients** (Ca, K, Na, Cl, Mg) ≈ 99.5% of biomass
- **Micronutrients** (B, F, Si, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Se, Mo, Sn, I) also necessary (≈99.99%)
- **Toxics**: Be, Al, As, Cd, Hg, Pb

Five Questions for Each Biogeochemical Cycle

1. What is the **importance** of this cycle to life?
2. What different **chemical forms** (species) are involved?
3. What are the main **processes and chemical reactions**?
4. What are the **stocks and flows** of the element in its different forms?
5. What are the **human impacts** on the cycle?

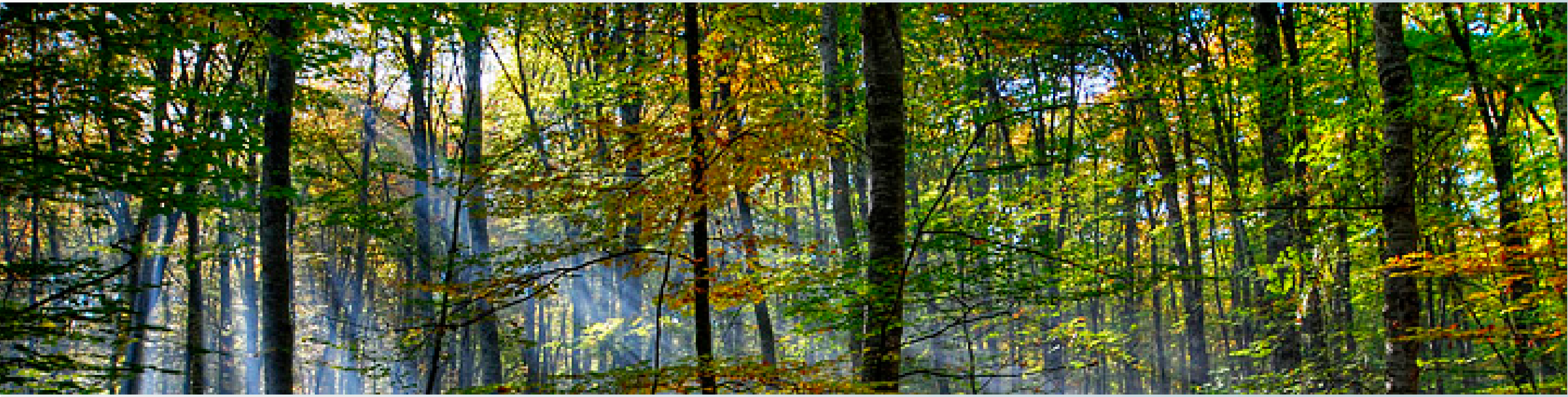
Generalized Biogeochemical Cycles



Biogeochemical Stocks
(1 Tg = 10^{18} g = 10^3 Gt)

	Atmosphere	Oceans	Sediments	Total
H_2O	17	1,400,000	190,000	1,600,000
C	0.8	40	70,000	70,000
N	3900	20	1000	4900
S	5×10^{-6}	1200	4000	5200
P	3×10^{-8}	0.1	80	80

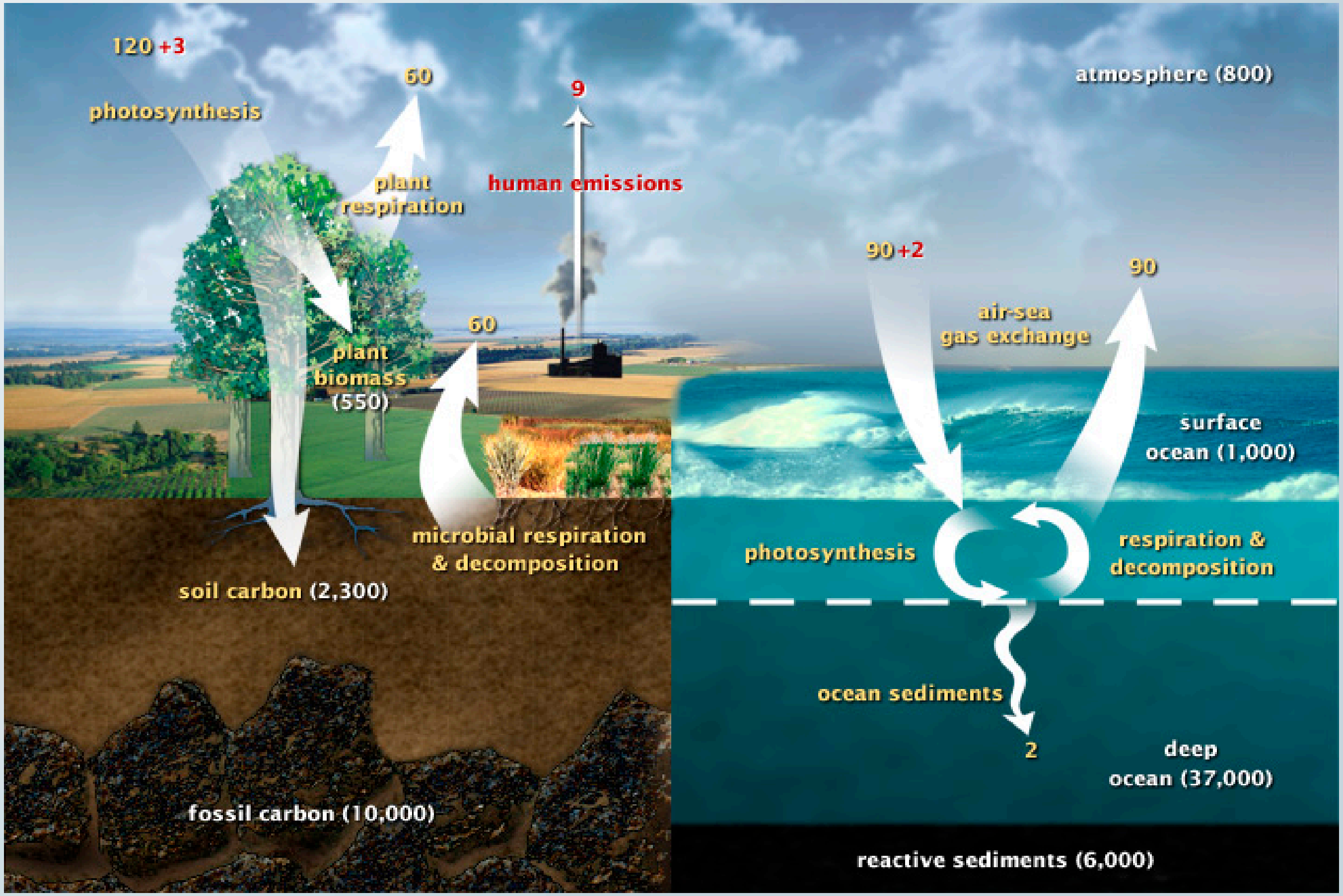
The Carbon Cycle



Carbon Cycle

The **carbon cycle** is the process by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the Earth.

The numbers are gigatons (Gt) of carbon per year. Yellow numbers are natural fluxes, red are human contributions, and white numbers indicate stored carbon.



http://en.wikipedia.org/wiki/Carbon_cycle

Carbon Reservoirs

- The global carbon cycle is usually divided into the following major reservoirs of carbon, interconnected by pathways of exchange:
  - The atmosphere
  - The terrestrial biosphere
  - The oceans, including dissolved inorganic carbon and living and non-living marine biota
  - The sediments, including fossil fuels, fresh water systems and non-living organic material, such as soil carbon
  - The Earth's interior, carbon from the Earth's mantle and crust. These carbon stores interact with the other components through geological processes

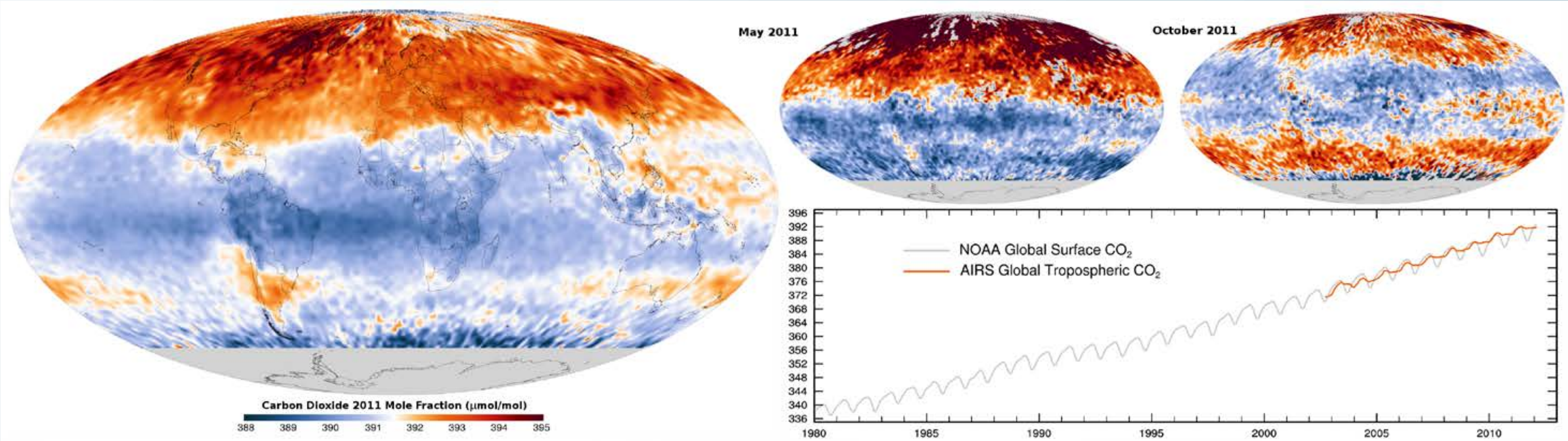
http://en.wikipedia.org/wiki/Carbon_cycle

Carbon Pools

http://en.wikipedia.org/wiki/Carbon_cycle

Pool	Quantity (gigatons)
Atmosphere	720
Oceans (total)	38,400
Total inorganic	*37,400*
Total organic	1,000
Surface layer	670
Deep layer	36,730
Lithosphere	
Sedimentary carbonates	> 60,000,000
Kerogens	15,000,000
Terrestrial biosphere (total)	2,000
Living biomass	600 - 1,000
Dead biomass	1,200
Aquatic biosphere	1 - 2
Fossil fuels (total)	4,130
Coal	3,510
Oil	230
Gas	140
Other (peat)	250

Atmospheric Carbon



http://en.wikipedia.org/wiki/Atmospheric_carbon_cycle

Atmospheric Carbon

- Approximately 720 Gt of carbon
- Two main forms: carbon dioxide, CO_2, and methane, CH_4.
  - CO_2 leaves the atmosphere through
    - plant photosynthesis, entering the terrestrial and oceanic biospheres.
    - dissolving in rain and directly in bodies of water (oceans, lakes, etc.).
    - absorption by rocks through weathering
  - CH_4 is mainly produced by the digestion or decay of biological organisms.
  - Methane has an atmospheric lifetime of about eight years. It can be removed from the atmosphere through
    - Reaction with photochemically produced hydroxyl free radical (OH).
    - Entering the stratosphere, where it is destroyed
    - Being absorbed into soil sinks

http://en.wikipedia.org/wiki/Carbon_cycle

Carbon in Terrestrial Biosphere

- Living biomass holds between 600 and 1,000 Gt of carbon, most of which is wood, while some 1,200 Gt of carbon are stored in the terrestrial biosphere as dead biomass.
- Carbon stored in soil (about 1500 Gt, including about 1/3 inorganic carbon in substances such as calcium carbonate, $CaCO_3$)
- Forests hold 86% of the planet's terrestrial above-ground carbon, and forest soils also hold 73% of the planet's soil carbon.
- Carbon leaves the terrestrial biosphere by
  - Combustion or respiration of organic carbon
  - Exported into the oceans through rivers

http://en.wikipedia.org/wiki/Terrestrial_biological_carbon_cycle

Biological Carbon Cycle Processes

Photosynthesis: $CO_2 + H_2O + \text{sunlight} \rightarrow CH_2O + O_2$

Respiration: $CH_2O + O_2 \rightarrow CO_2 + H_2O + 469$ kJ/mole C

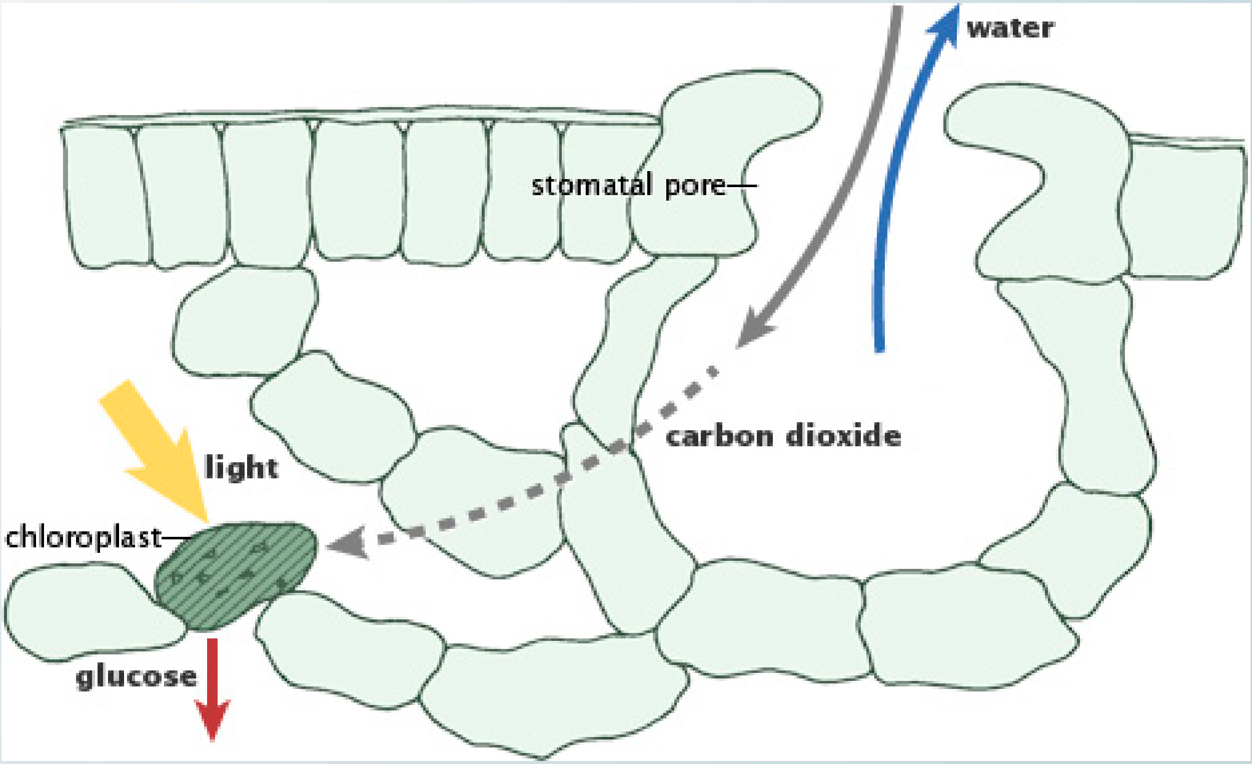
$$NPP = GPP - R_{autotrophic}$$

Fermentation: $CH_2O + H_2O \rightarrow 2H_2 + CO_2$

Methane bacteria: $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

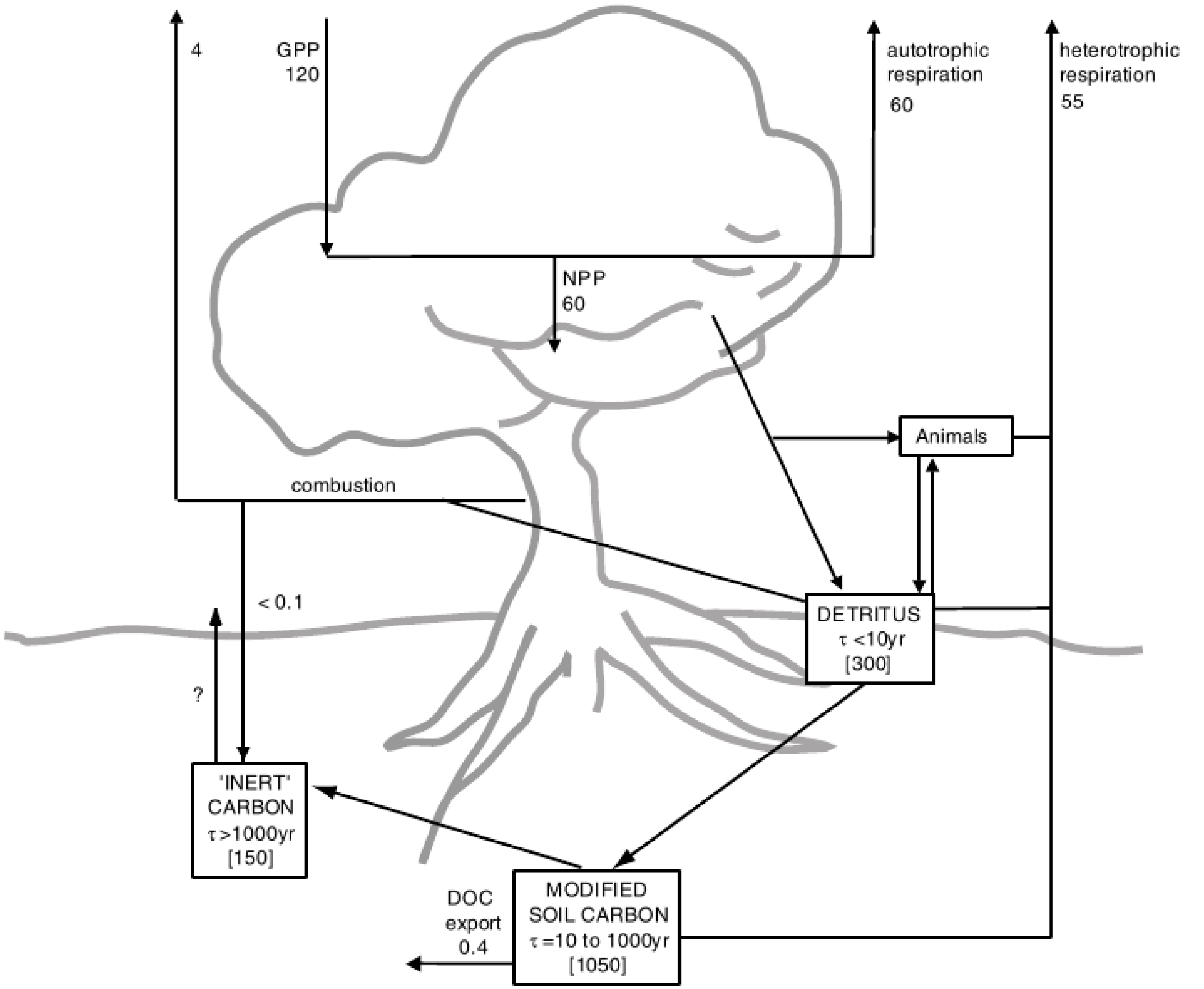
Acetate splitting: $CH_3COOH \rightarrow CO_2 + CH_4$

Atmospheric oxidation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$


water
stomatal pore
carbon dioxide
light
chloroplast
glucose

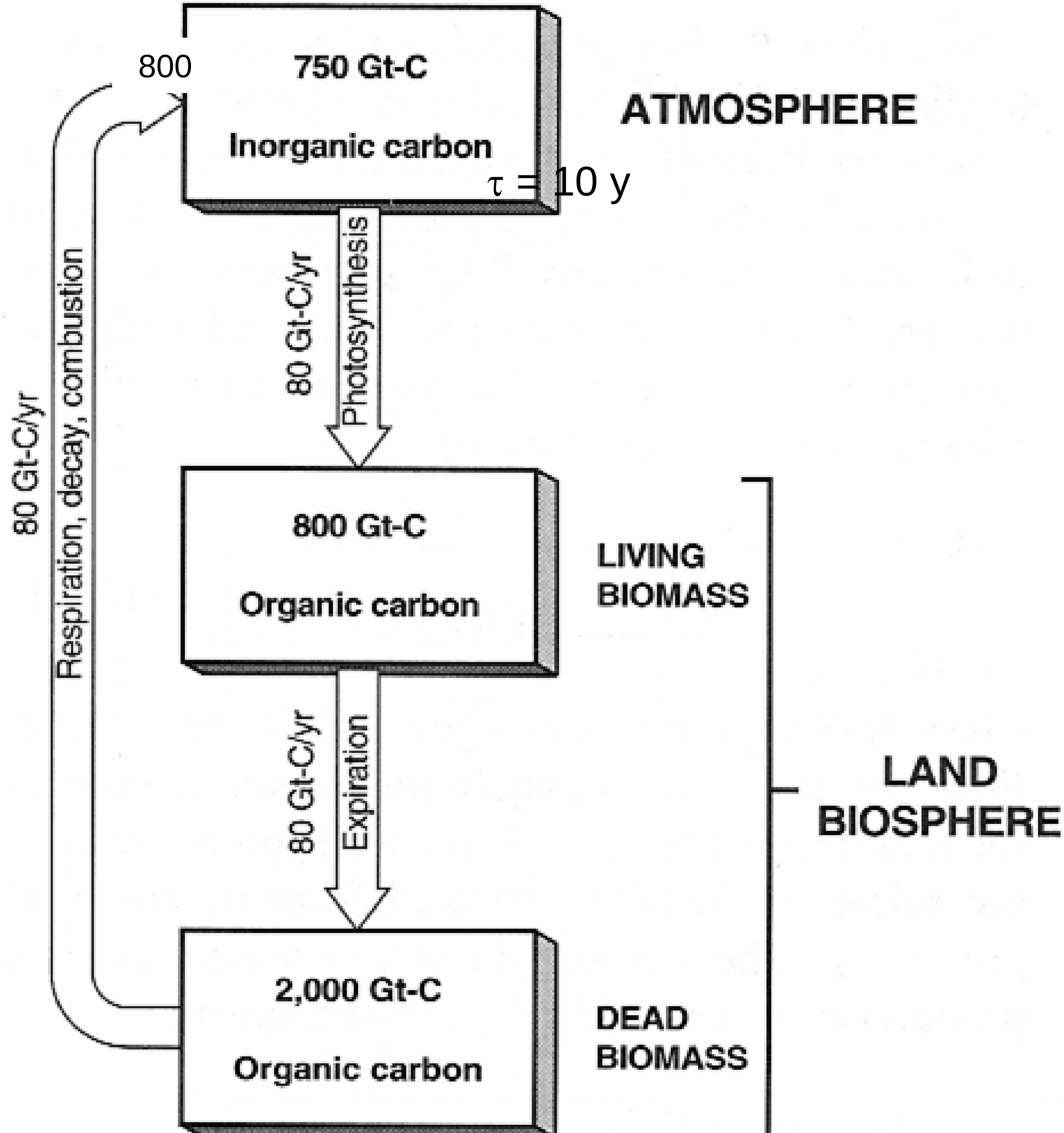
Carbon in Terrestrial Biosphere

CO_2 is removed from the atmosphere through gross primary production (GPP) and converted to organic carbon. About half of GPP is respired back into the atmosphere directly. The rest, the net primary production (NPP), stays in the ecosystem and is released into the atmosphere on different time scales through heterotrophic respiration or exported in water in the form of dissolved organic carbon (DOC). The units are gigatons.



http://en.wikipedia.org/wiki/Terrestrial_biological_carbon_cycle

Terrestrial Carbon Cycle Stocks and Flows



Turco

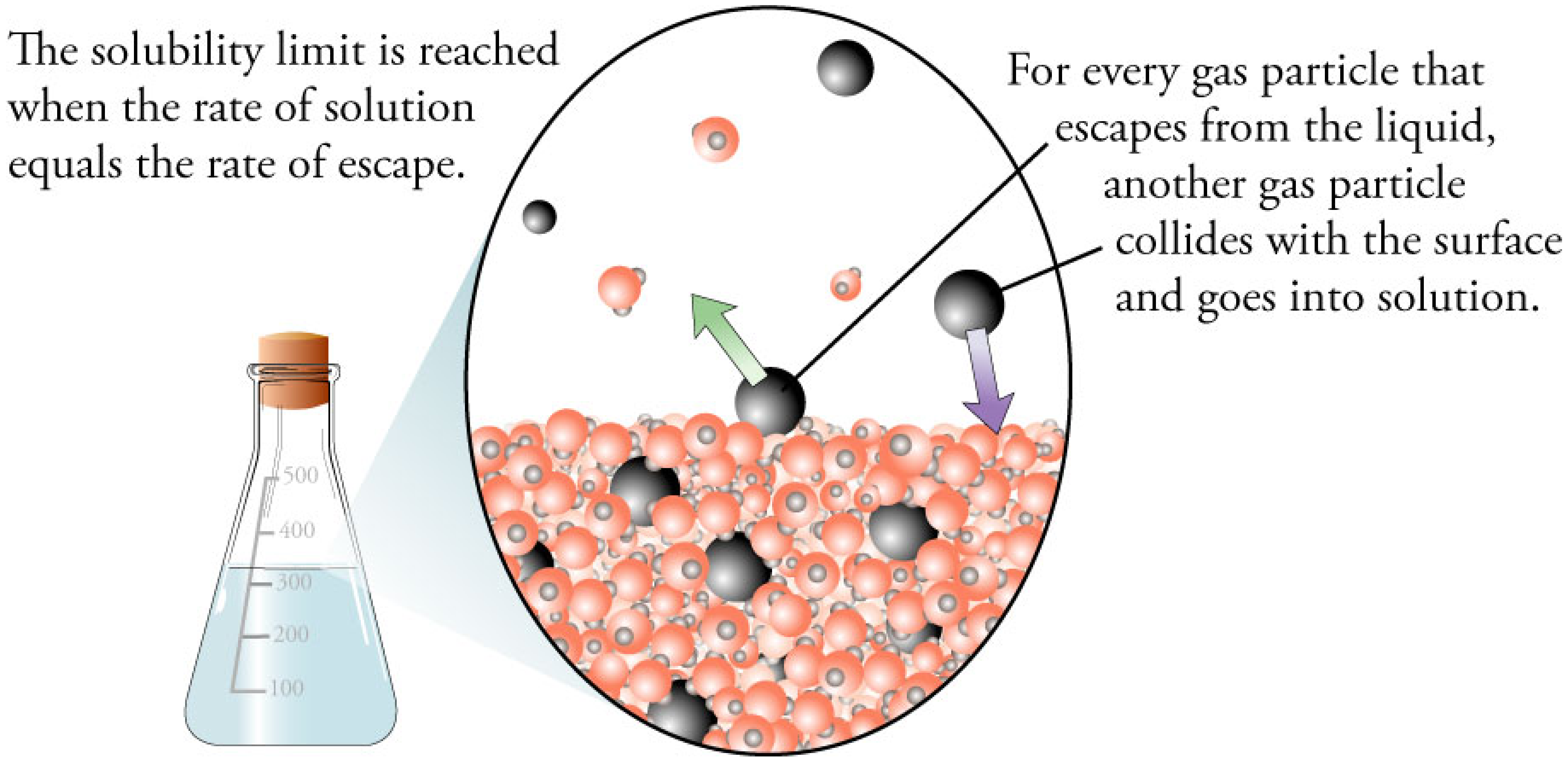
Oceanic Carbon

- Carbon enters the ocean mainly through solution of atmospheric carbon dioxide.

  $$CO_2(g) \rightleftharpoons CO_2(aq)$$

- The net rate of solution is determined by
  - the rate at which CO_2 molecules collide with the surface of the water and move into the water (R_{soln})
  - the rate at which CO_2 escapes from the water into the atmosphere (R_{escape}) , which is determined by the concentration of CO_2 in the water and the temperature of the water.
- If these two rates are equal, the system will be in equilibrium with no net change in the concentrations of CO_2 in the ocean or the atmosphere.

Dynamic Equilibrium for Gas Dissolved in Liquid



Gas Solubility

Add a gas above a liquid in a closed container

↓

Initially, the rate of solution is greater than the rate of escape → Net shift of particles into solution

↓

Increased rate of escape… ← Increased concentration of dissolved gas

↓

…Until the rate of escape equals rate of solution → Constant changes between dissolved and undissolved gas, but no net change in amount of either

Dynamic equilibrium (solubility limit) ←

Partial Pressure and Gas Solubility

- As the concentration of CO_2 in the atmosphere increases, the ocean absorbs more CO_2.
- Increased concentration of CO_2 in the atmosphere leads to an increase in the rate of collisions with the ocean, increasing the rate of solution, disrupting the dynamic equilibrium, making the $R_{soln} > R_{escape}$, and leading to a net shift of CO_2 into the ocean.

$\boxed{\text{Increased partial pressure of a gas over a liquid in a system initially at dynamic equilibrium (Rate of solution = Rate of escape)}}$

↓

Increased rate of collision between gas particles and liquid ⟶ Increased rate of solution

↓

Net movement of gas particles into solution ← Rate of solution greater than rate of escape

↓

Increased concentration of solute in solution ⟶ Increased rate of escape until it equals the higher rate of solution

↙

$\boxed{\text{Greater solubility}}$

Temperature and Gas Solubility

- Like other gases, increased temperature leads to decreased solubility of CO_2.
- Background
  - Two factors determine whether a change is spontaneous.
    - Exothermic reactions are more likely to be spontaneous than endothermic reactions.
    - Changes that lead to greater dispersal of matter and energy (increased entropy) are more likely than changes that lead to less dispersed states.
  - Molecules in solution have attractions to other particles, but molecules in the gas form have almost no attractions. Therefore, when CO_2 dissolves in the ocean it forms attractions, making the molecules more stable and releasing energy. Therefore, the solution of CO_2 is exothermic and escape of CO_2 is endothermic.
  - Particles in the gas form are more dispersed than in solution.

Effect of Increased Temperature on Gas Solubility

- Increased temperature favors endothermic changes
  - Increased temperature increases the rate of solution and rate of escape, but it has a greater effect on the endothermic rate of escape. Therefore, increased temperature increases the net rate of escape of CO_2 into the atmosphere.
- Increased temperature favors more dispersed states.
  - Increased temperature makes it easier for the CO_2 molecules to move back and forth between solution and gas, and because there are more ways to arrange particles in the more dispersed gas, probability predicts that the CO_2 will move into the gas form.
- The escape of CO_2 into the atmosphere is favored by both factors.

CO_2 and Ocean Acidity

- CO_2 molecules react with water to form carbonic acid, which ionizes to form hydronium, hydrogen carbonate, and carbonate ions.

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

- The absorption of anthropogenic CO_2 has acidified the surface layers of the ocean, with a steady decrease of 0.02 pH units per decade over the past 30 years and an overall decrease since the pre-industrial period of 0.1 pH units.
- Although these increases appear small in terms of pH, they are associated with a substantial changes in ocean chemistry.

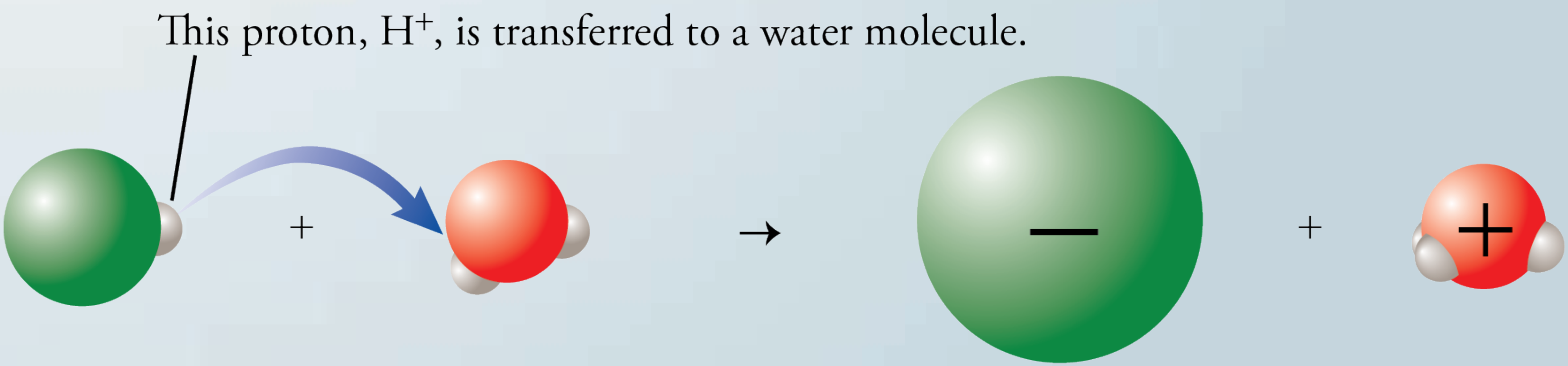
O Hoegh-Guldberg, J F Bruno Science 2010;328:1523-1528

Arrhenius Acids

- An ***acid*** is a substance that generates hydronium ions, H_3O^+ (often described as H^+), when added to water.
- An ***acidic solution*** is a solution with a significant concentration of H_3O^+ ions.
- Characteristics of acids
  - sour taste.
  - turn litmus from blue to red.
  - react with bases.

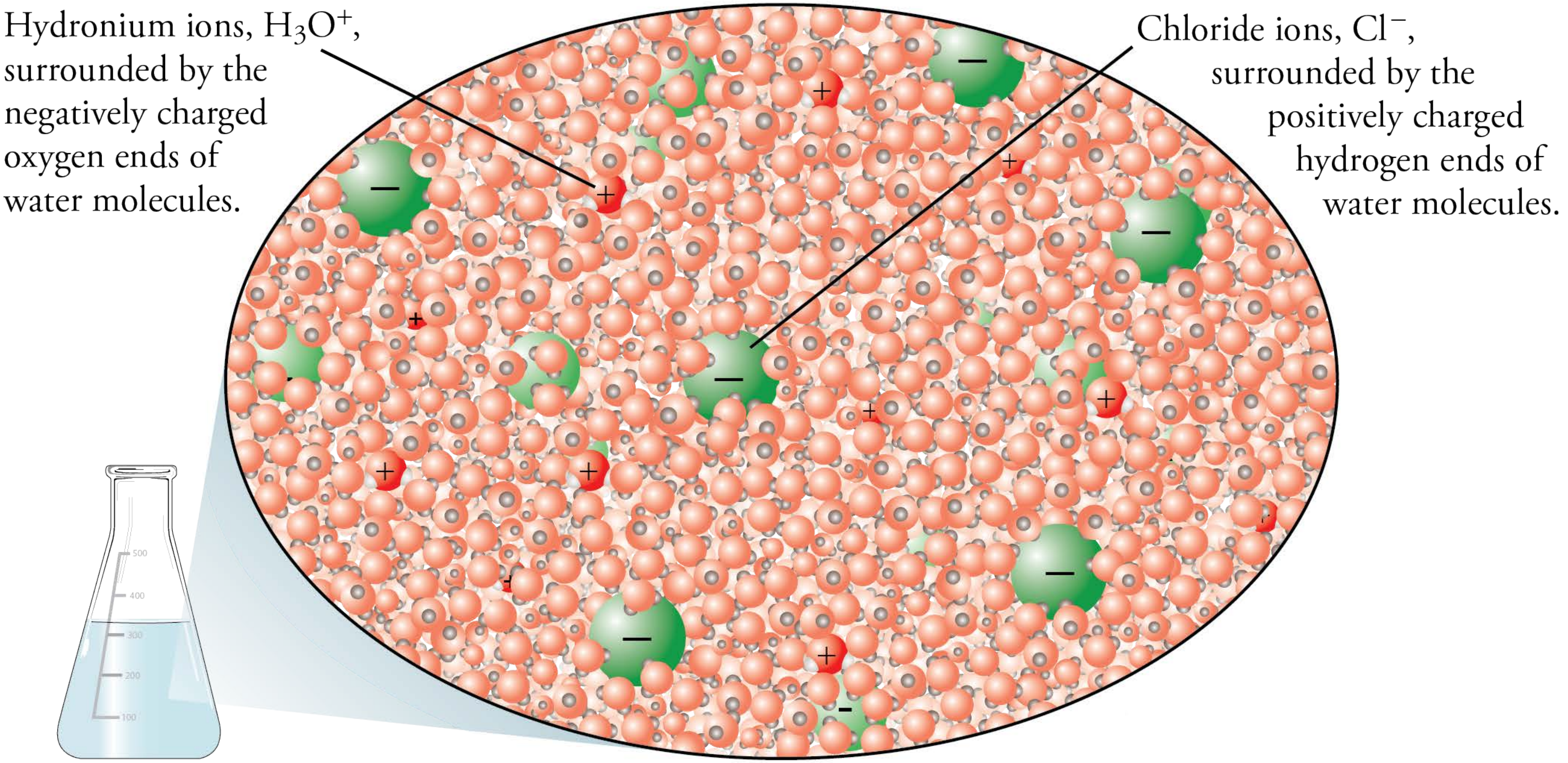
Strong Acid and Water

When HCl dissolves in water, hydronium ions, H_3O^+, and chloride ions, Cl^-, ions form.

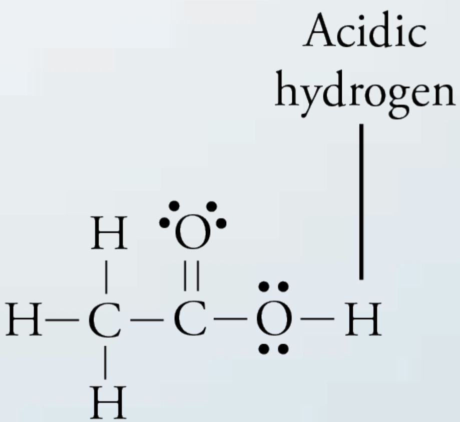


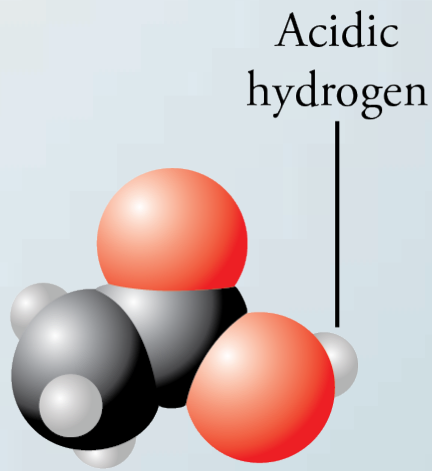
$$HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

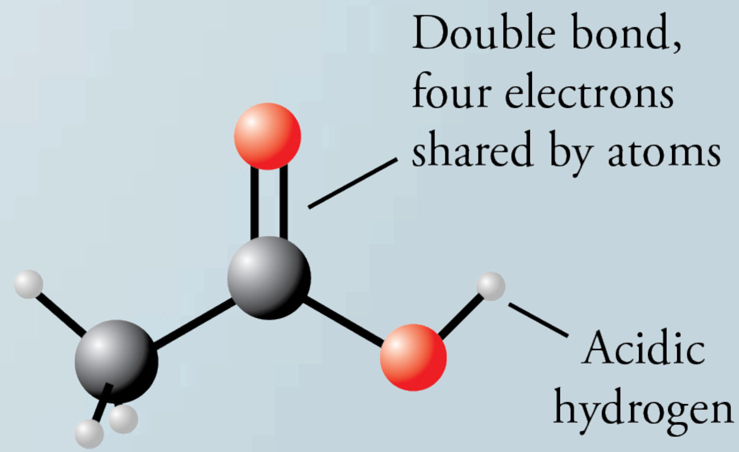
Solution of a Strong Acid



Acetic Acid


Acidic
hydrogen
H
H—C—C—O—H
H
O


Acidic
hydrogen

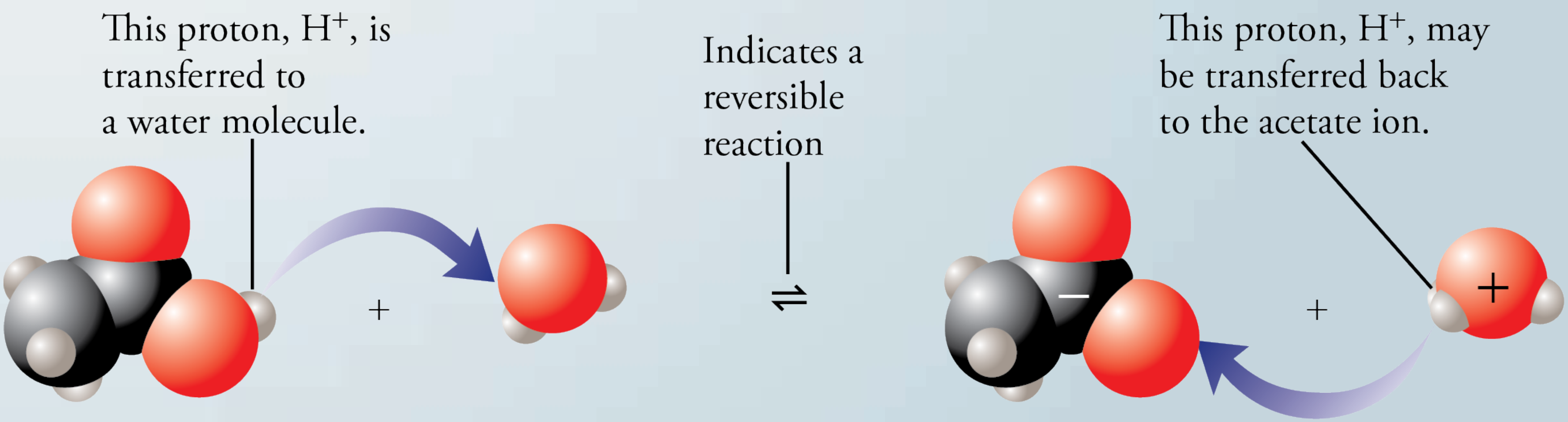

Double bond,
four electrons
shared by atoms
Acidic
hydrogen

Strong and Weak Acids

- ***Strong Acid*** = due to a completion reaction with water, generates close to one H_3O^+ for each acid molecule added to water.
- ***Weak Acid*** = due to a reversible reaction with water, generates significantly less than one H_3O^+ for each molecule of acid added to water.

Weak Acid and Water

Acetic acid reacts with water in a reversible reaction, which forms hydronium and acetate ions.

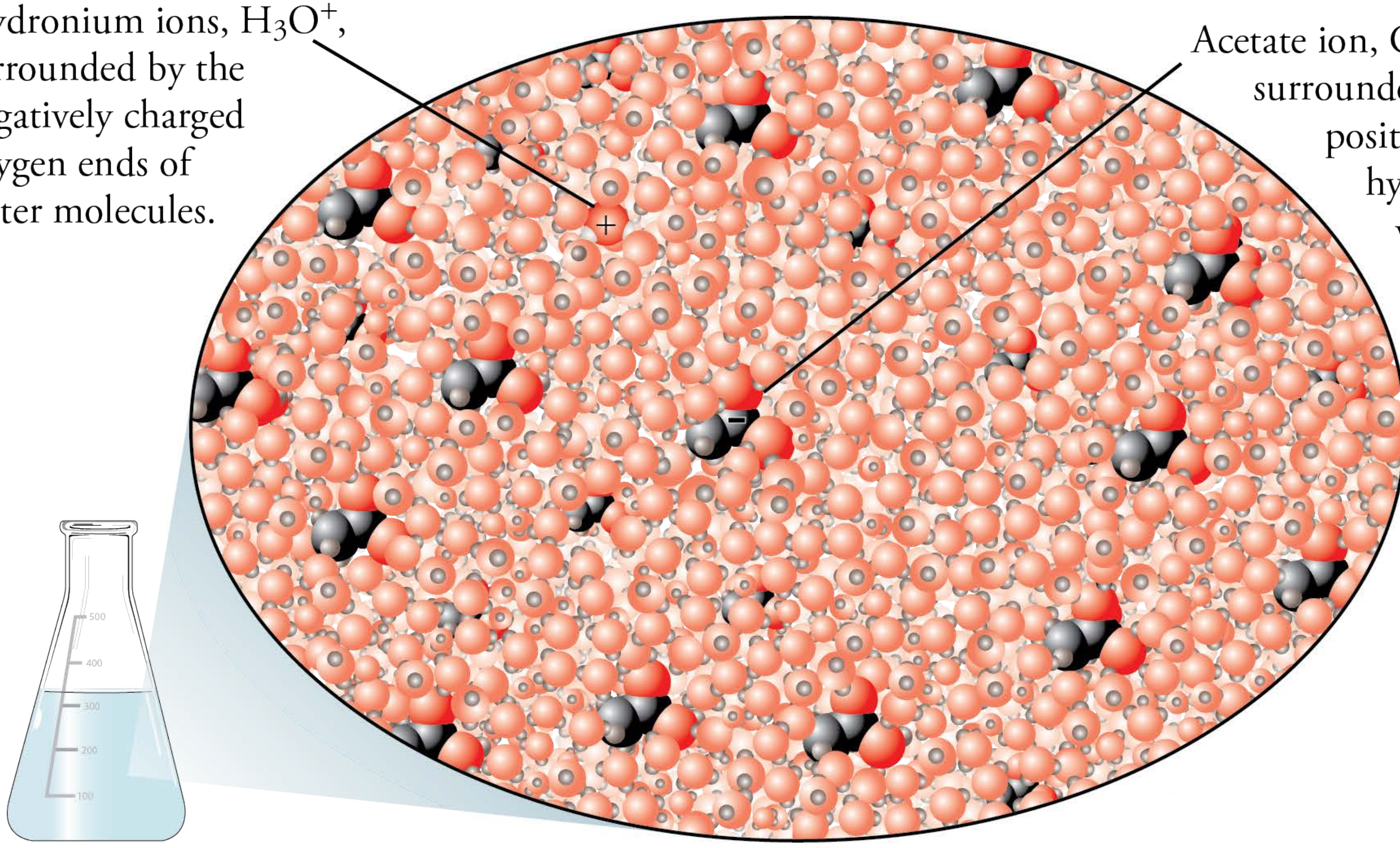


$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+(aq)$$

Solution of Weak Acid

In a typical acetic acid solution, there are about 250 times as many uncharged acetic acid molecules, $HC_2H_3O_2$, as acetate ions, $C_2H_3O_2^-$.

Hydronium ions, H_3O^+, surrounded by the negatively charged oxygen ends of water molecules.



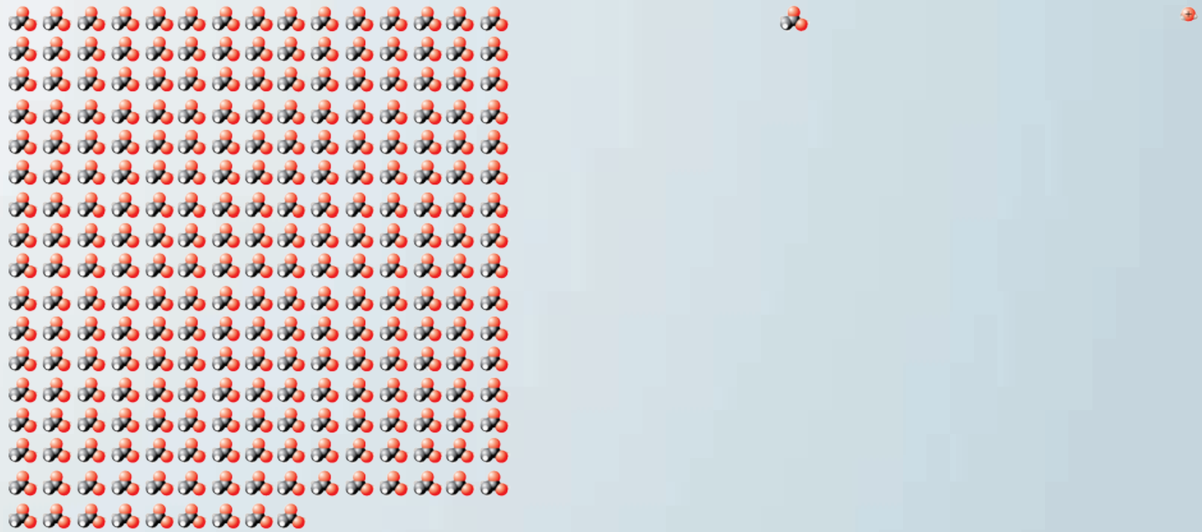
Acetate ion, $C_2H_3O_2^-$, surrounded by the positively charged hydrogen ends of water molecules.

Strong and Weak Acids

For every 250 molecules of the weak acid acetic acid, $HC_2H_3O_2$, added to water, there are about

$$HC_2H_3O_2(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad C_2H_3O_2^{\,-}(aq) \quad + \quad H_3O^+(aq)$$

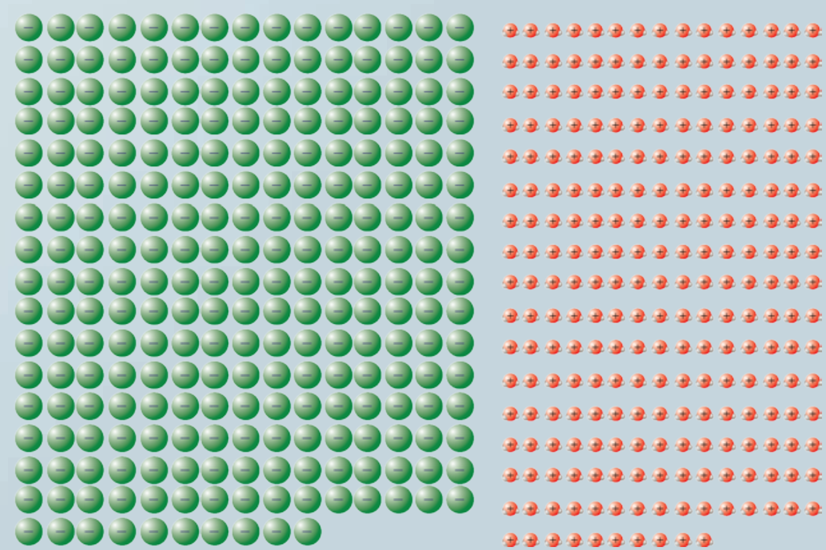
249 uncharged acetic acid molecules	One acetate ion	One hydronium ion



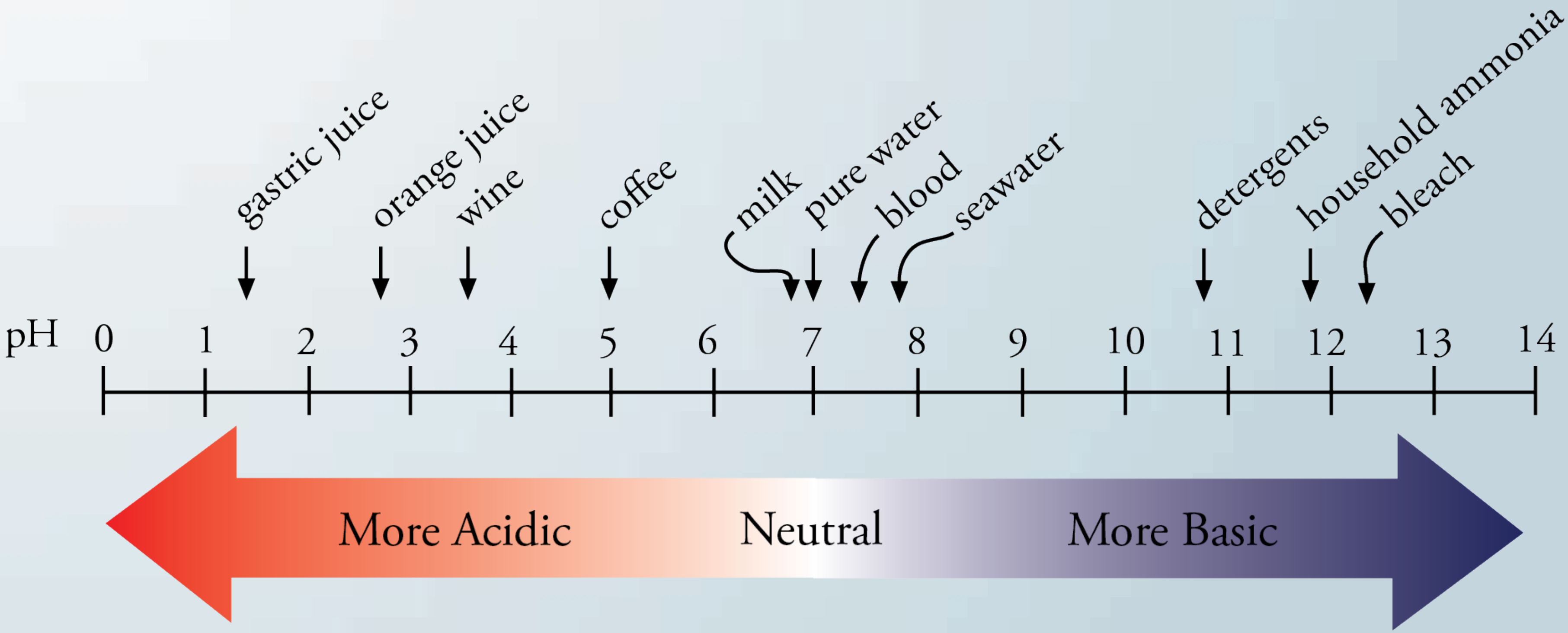
For every 250 molecules of the strong acid hydrochloric acid, HCl, added to water, there are about

$$HCl(g) \quad + \quad H_2O(l) \quad \rightarrow \quad Cl^-(aq) \quad + \quad H_3O^+(aq)$$

Zero uncharged HCl molecules	250 chloride ions	250 hydronium ions



pH Range



Acidic solutions have pH values less than 7.

Basic solutions have pH values greater than 7.

Oceanic Carbon Cycle

- CO_2 is absorbed from the atmosphere and converted into dissolved inorganic carbon (DIC).
- DIC is converted by phytoplankton into organic carbon.
  - About half of the GPP is respirated and converted back into DIC.
  - The rest stays in the form of net primary production (NPP).
- Some of the organic carbon sinks into the lower ocean levels as detritus or calcium carbonate in shells.
- Some soft tissue is converted into particulate organic carbon or dissolved organic carbon and, from these forms, into dissolved inorganic carbon. The rest sinks to the ocean floor.

http://en.wikipedia.org/wiki/Oceanic_carbon_cycle

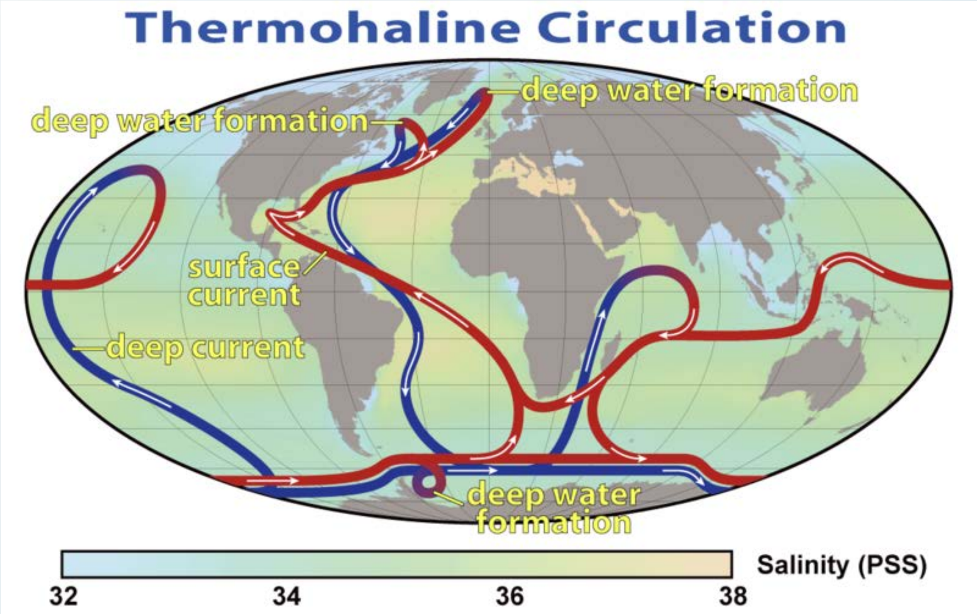
Oceanic Carbon

- The oceans contain about 36,000 Gt of carbon, mostly in the form of bicarbonate ion, HCO_3^- (over 90%, with most of the remainder being carbonate, CO_3^{2-}).
- The balance of dissolved inorganic carbon (DIC) : dissolved organic carbon (DOC) : particle organic carbon is about 2000:38:1.

http://en.wikipedia.org/wiki/Oceanic_carbon_cycle

Oceanic Carbon Cycle

- Thermohaline circulation can bring carbon in the deep ocean levels to the upper levels, where it can again be exchanged with the atmosphere. Thermohaline circulation is a part of the large-scale ocean circulation that is driven by global density gradients created by surface heat and freshwater fluxes.



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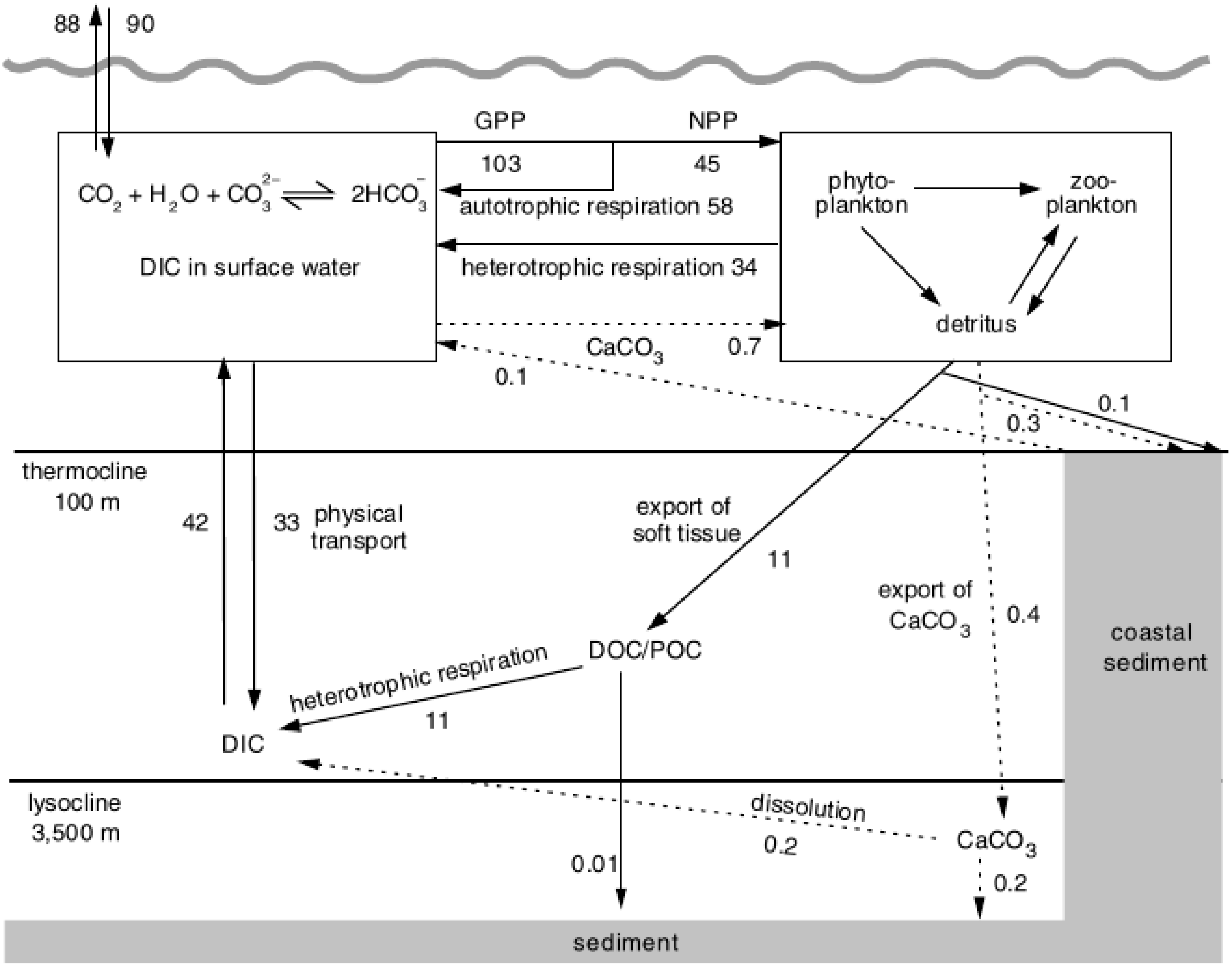
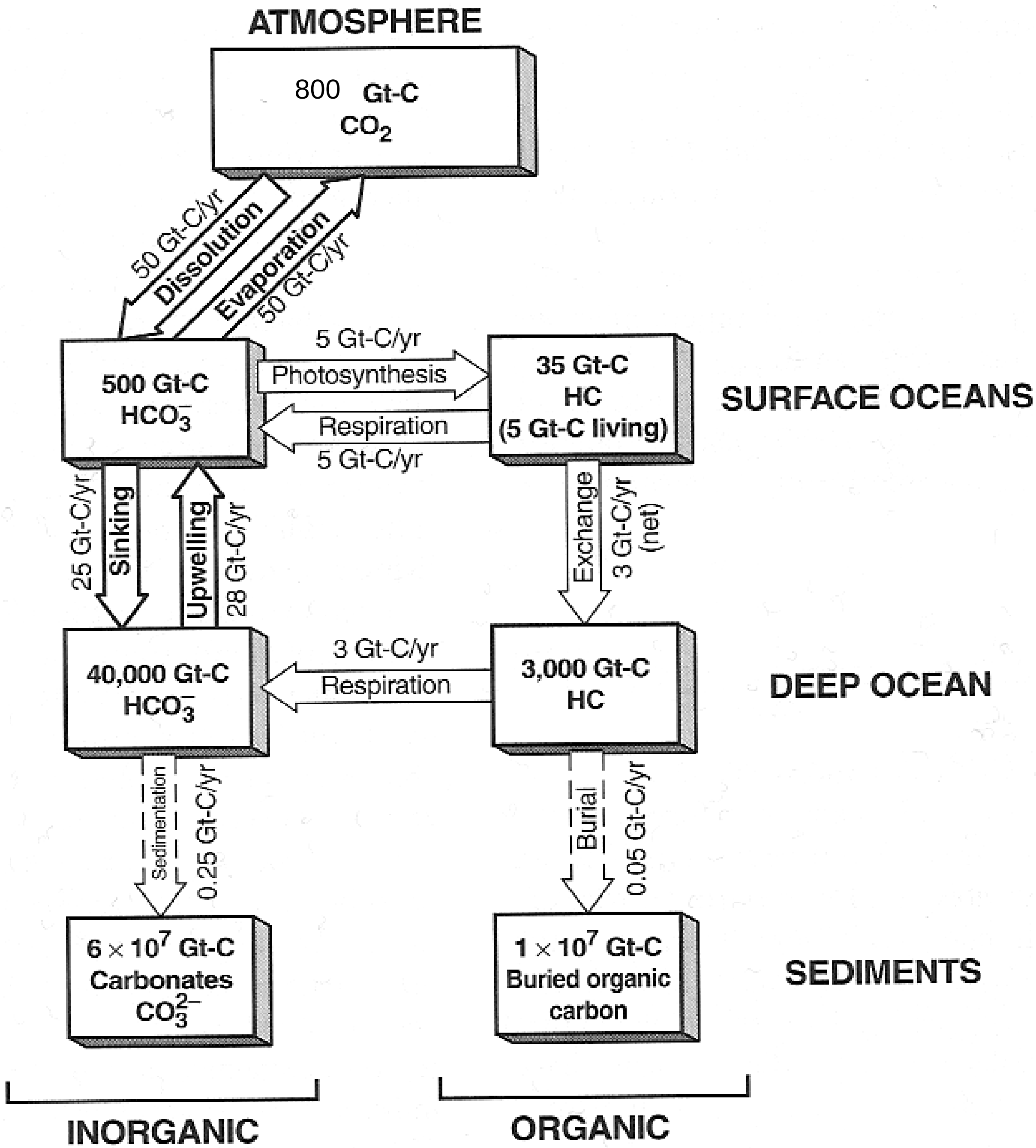
Oceanic Carbon



http://en.wikipedia.org/wiki/Oceanic_carbon_cycle

Ocean Carbon Cycle Stocks and Flows

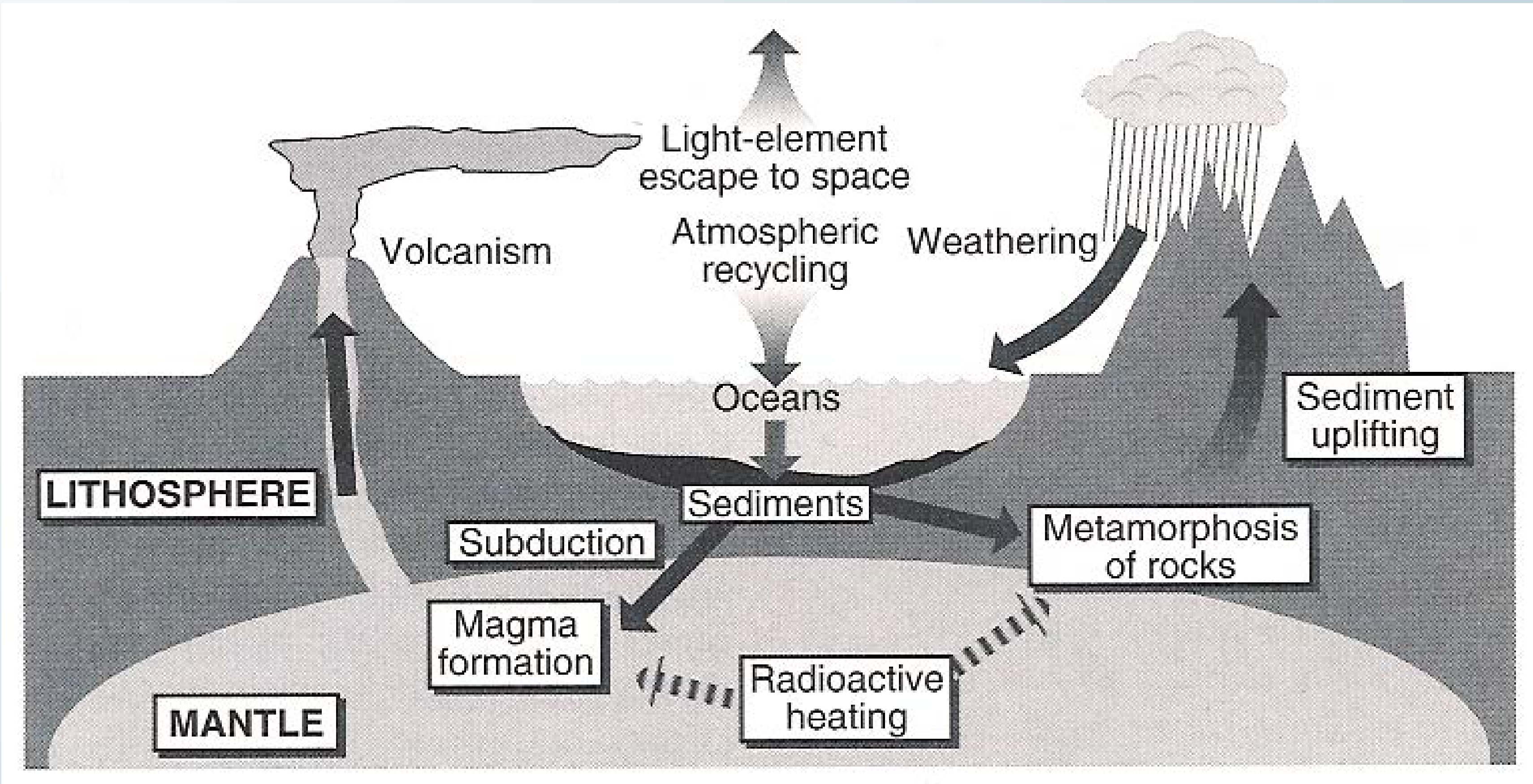


Geological Carbon Cycle

- Most of the earth's carbon is stored inertly in the Earth's lithosphere.
- About 80% is limestone and its derivatives, which form from the sedimentation of calcium carbonate stored in the shells of marine organisms.
- About 20% is stored as kerogens formed through the sedimentation and burial of terrestrial organisms under high heat and pressure.
- Carbon can leave the geosphere in several ways.
  - Metamorphosis of carbonate rocks when they are subducted into the earth's mantle.
  - Released into the atmosphere and ocean through volcanoes and hotspots.
  - Removed by humans through the direct extraction of kerogens in the form of fossil fuels.

http://en.wikipedia.org/wiki/Carbon_cycle

Large-Scale Geological Processes



Geological Carbon Cycle Processes

Atmosphere–ocean exchange: CO_2 (gas) $\rightleftharpoons$ CO_2 (aq)

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

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

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

Shell building, dissolution: $Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$

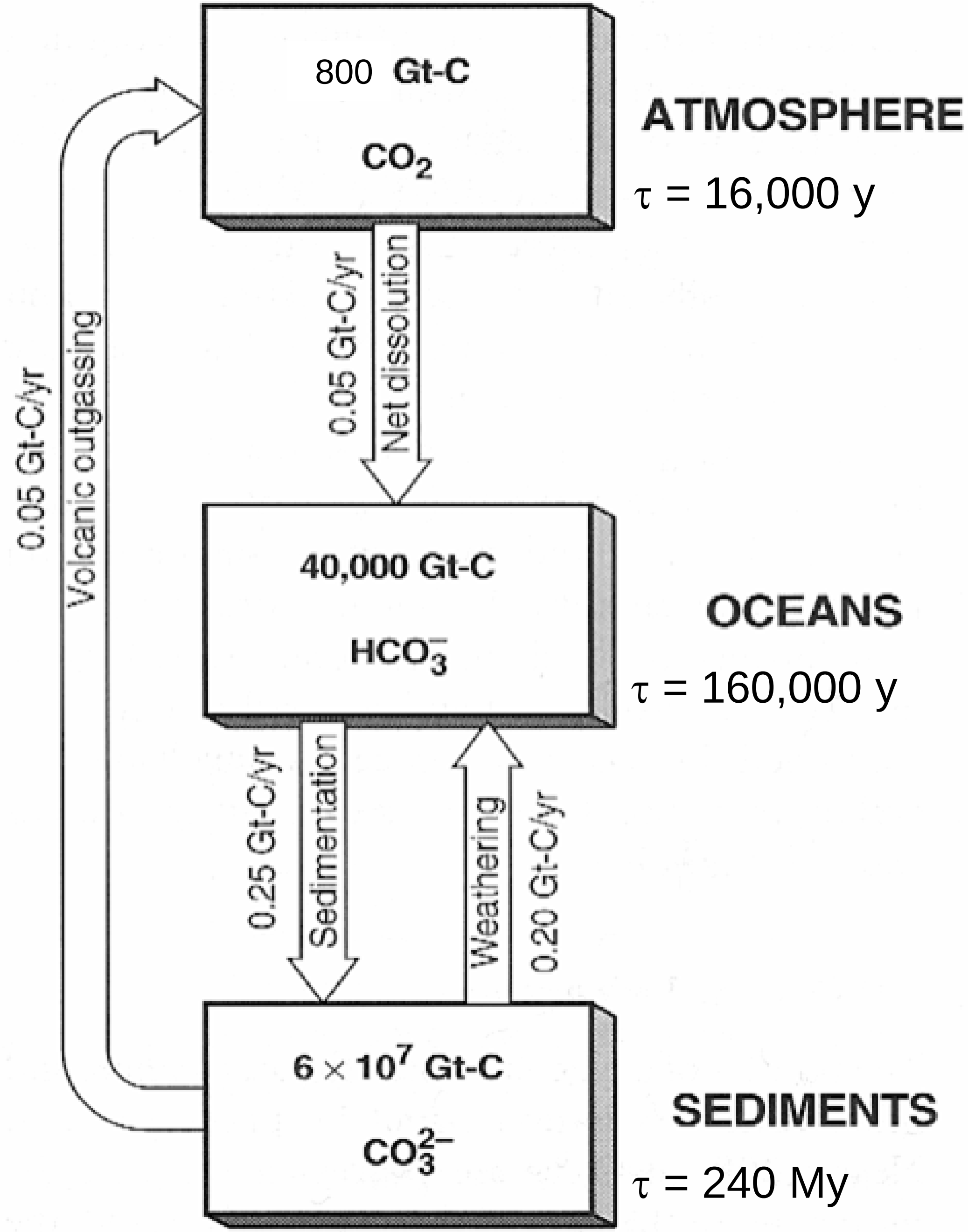
Weathering: $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$

Weathering: $CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + SiO_2 + 2HCO_3^-$

Silicate reconstitution: $CaCO_3 + SiO_2 + \text{heat} \rightarrow CaSiO_3 + CO_2$

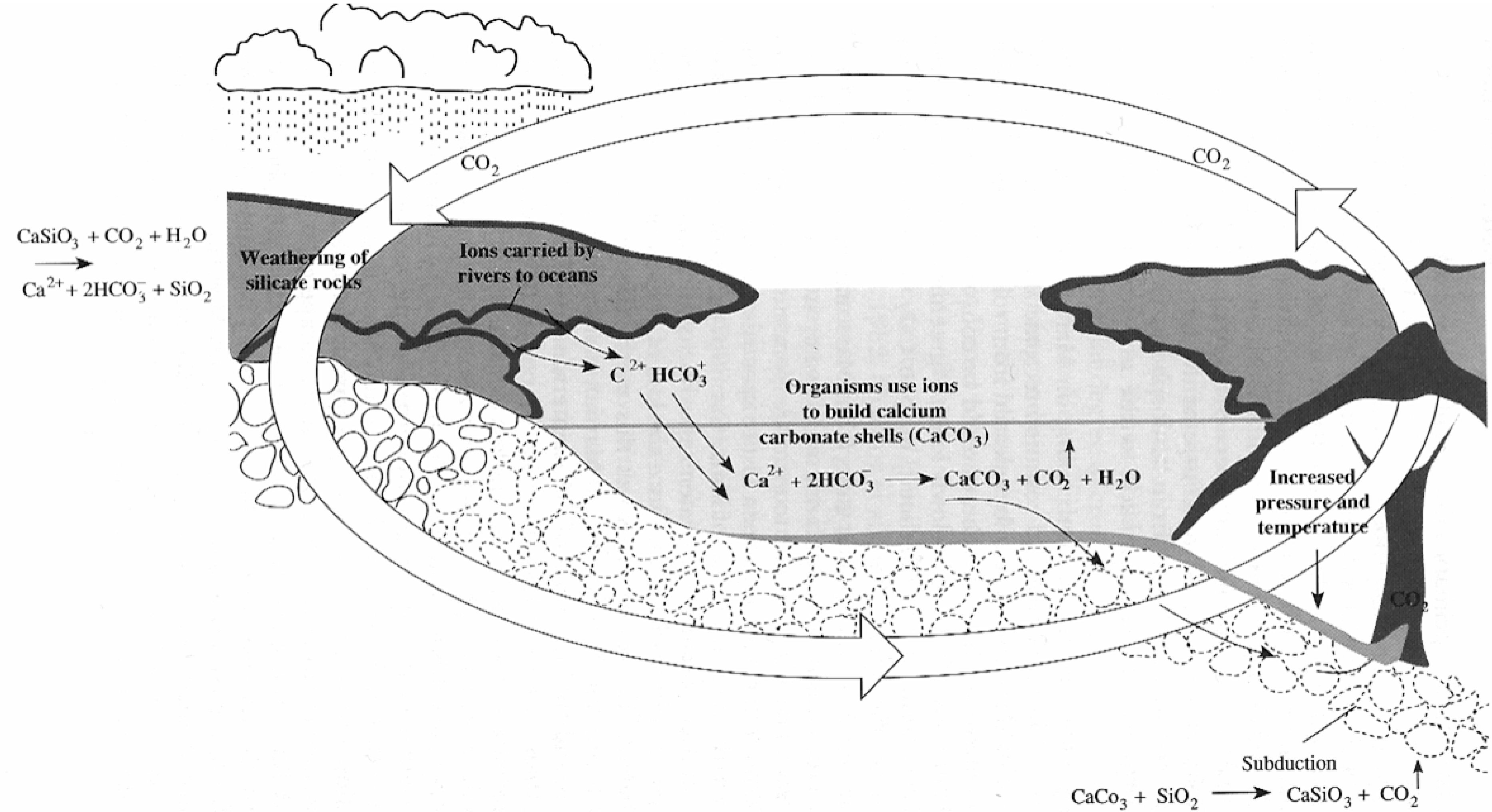
Volcanism: CO_2 (rock) $\rightarrow$ CO_2 (atm)

Geological Carbon Cycle Stocks and Flows



Turco

Geological Carbon Cycle



Origin of Fossil-fuel (Oil & Gas) Deposits

- **Petroleum** or **crude oil** = a naturally occurring flammable liquid consisting of a complex mixture of hydrocarbons and other liquid organic compounds, that are found in geologic formations beneath the Earth's surface.
- A fossil fuel, it is formed when large quantities of dead organisms, usually zooplankton and algae, are buried underneath sedimentary rock and undergo intense heat and pressure.

http://en.wikipedia.org/wiki/Petroleum

Origin of Fossil-fuel (Oil & Gas) Deposits

- Three conditions must be present for oil reservoirs to form:
  - a source rock rich in hydrocarbon material buried deep enough for subterranean heat to cook it into oil;
  - a porous and permeable reservoir rock for it to accumulate in;
  - and a cap rock (seal) or other mechanism that prevents it from escaping to the surface.

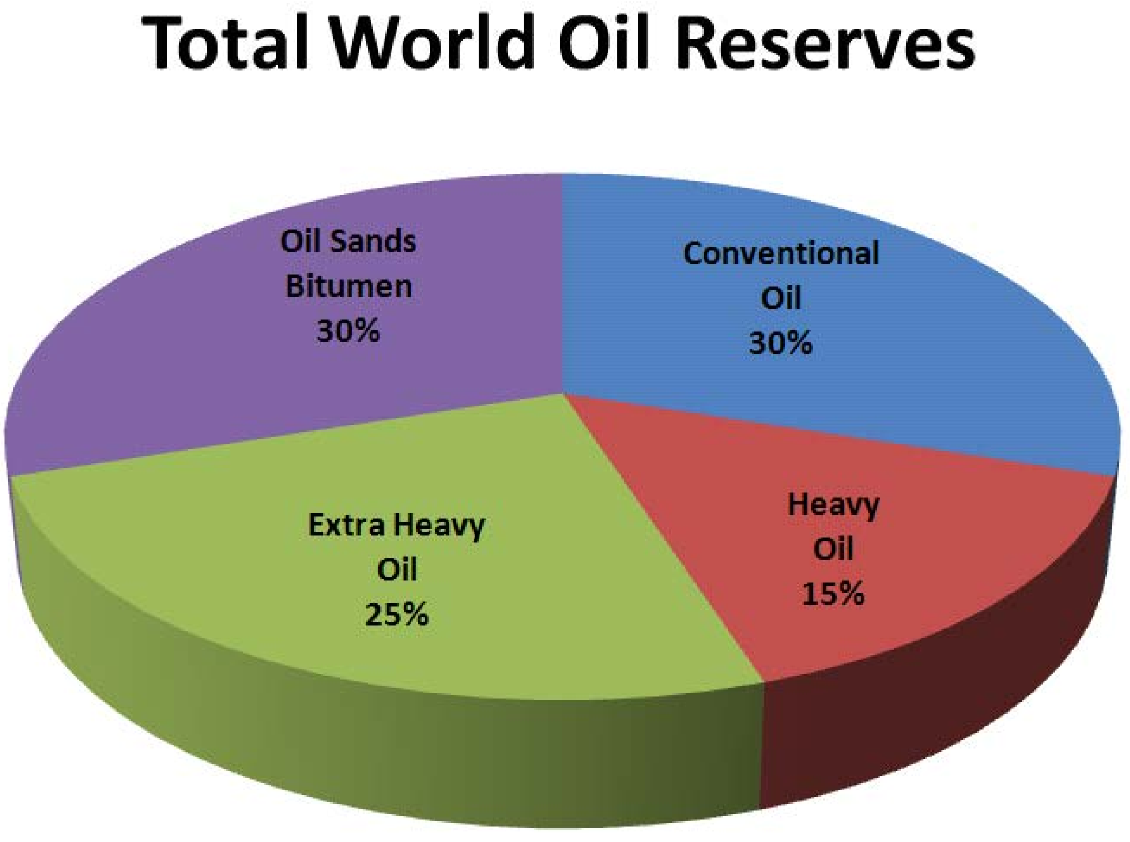
http://en.wikipedia.org/wiki/Petroleum

Unconventional Petroleum

- **Heavy crude oil** or **extra heavy crude oil** is any type of crude oil which does not flow easily.
  - Production, transportation, and refining of heavy crude oil present special challenges compared to light crude oil.
- **Oil sands, tar sands** or, more technically, **bituminous sands,** are loose sand or partially consolidated sandstone containing naturally occurring mixtures of sand, clay, and water, saturated with a dense and extremely viscous form of petroleum technically referred to as bitumen (or colloquially tar due to its similar appearance, odor and color).
  - Natural bitumen deposits are reported in many countries, but in particular are found in extremely large quantities in Canada.

http://en.wikipedia.org/wiki/Petroleum

World Petroleum Reserves

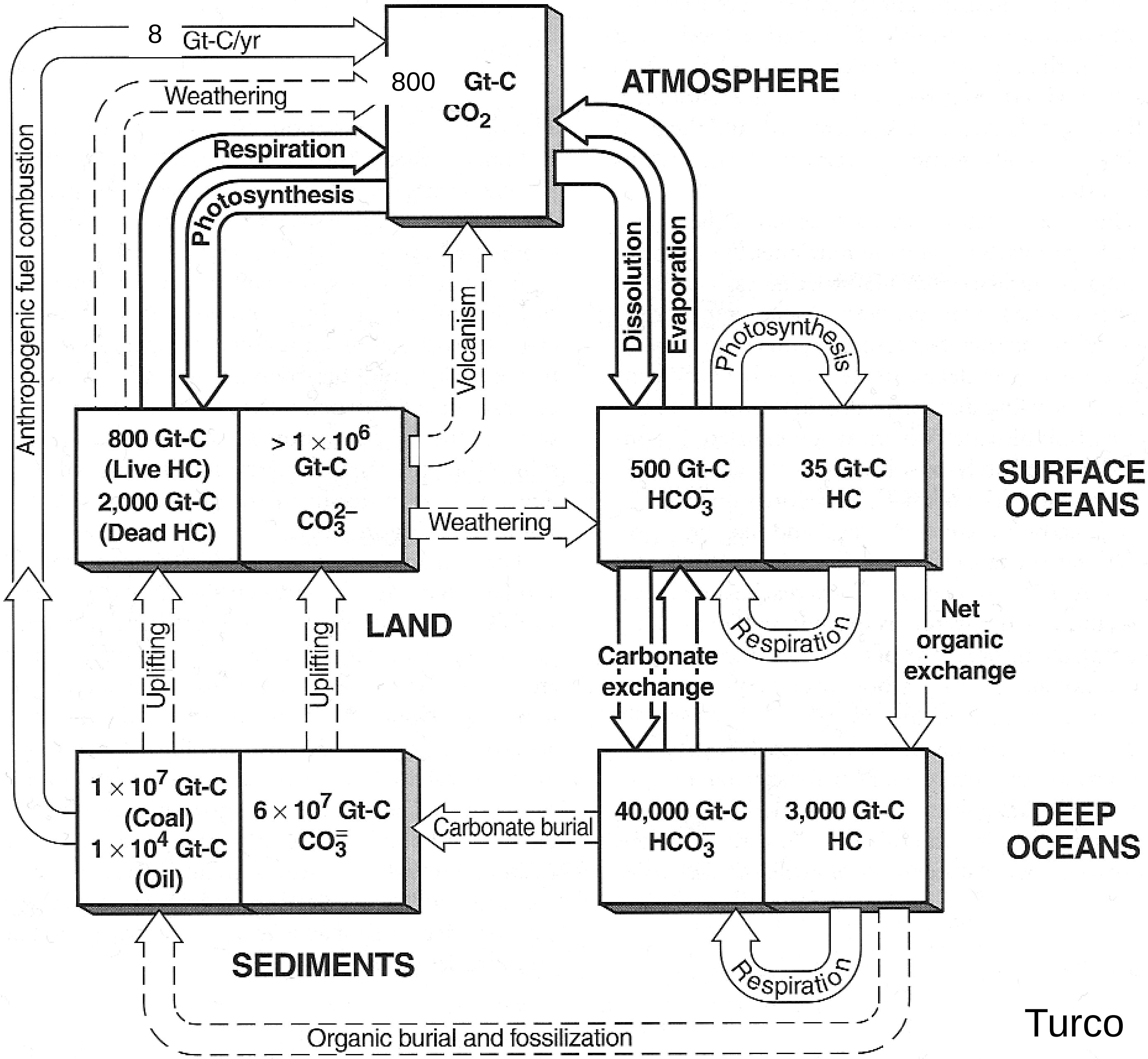


http://en.wikipedia.org/wiki/Petroleum

Fossil Fuel Stocks

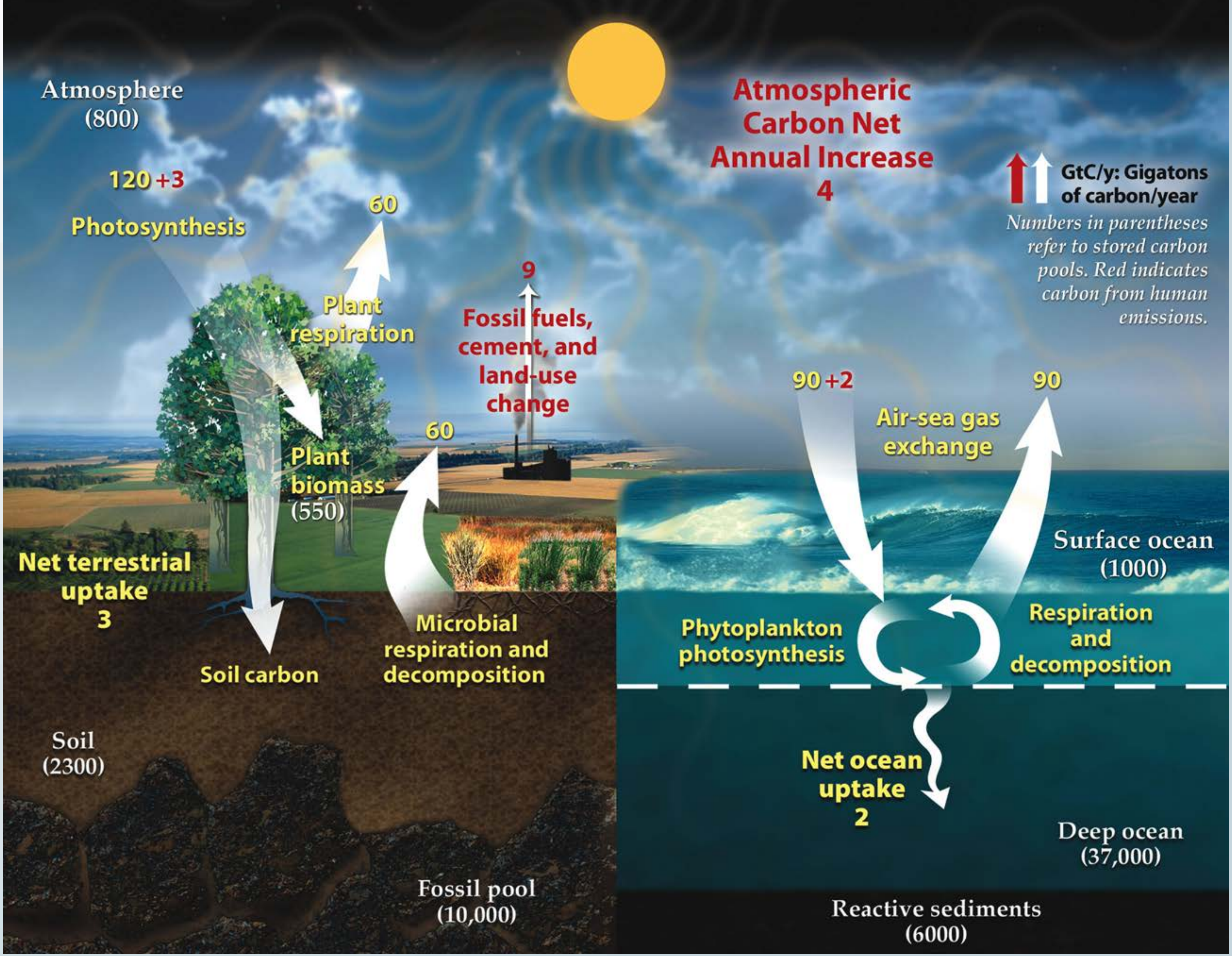
Type	Recoverable Stocks (GtC)	
	median estimate	low – high estimates
Oil	200	160 – 400
Gas	150	110 – 350
Coal	2,500	1,500 – 6,500
Methane hydrate	10,000	300 – 600,000
Oil Shale	40,000	?
Total sequestered organic carbon	10,000,000	?

Grand Carbon Cycle



Turco

Unbalanced Carbon Cycle due to Human Activity



Human Influence

- Direct emissions from burning fossil fuels
- Indirectly by changing the terrestrial and oceanic biosphere.
  - Land use and land cover change has led to the loss of biodiversity, which lowers ecosystems' resilience to environmental stresses and decreases their ability to remove carbon from the atmosphere.
  - Deforestation for agricultural purposes removes forests...more carbon stays in the atmosphere.
  - Air pollution damages plants
  - Agricultural and land use practices lead to higher erosion rates, decreasing plant productivity.
- Higher temperatures increase decomposition rates in soil, returning CO_2 more quickly to the atmosphere.

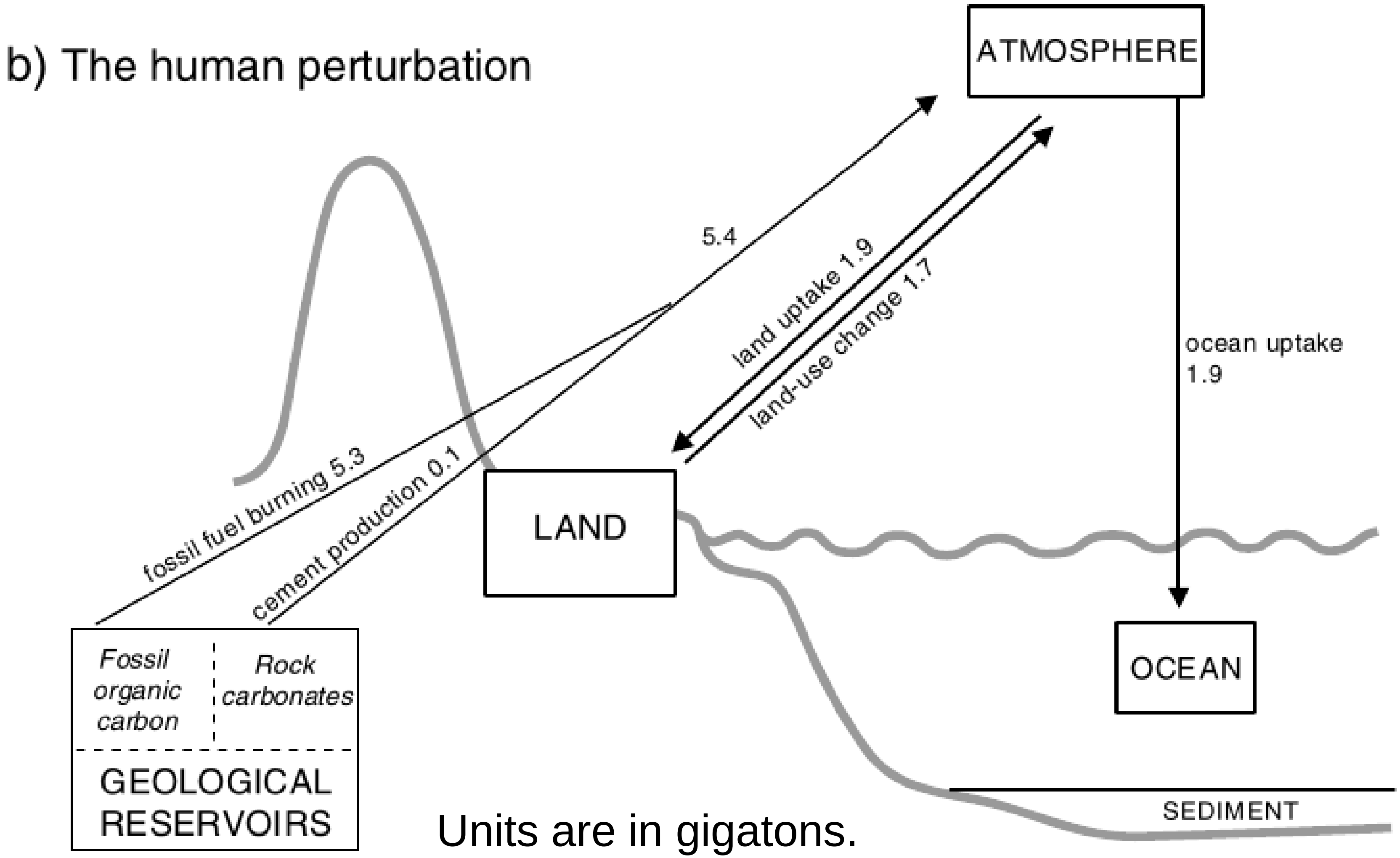
http://en.wikipedia.org/wiki/Carbon_cycle

Human Influence

- Increased levels of CO_2 in the atmosphere increases photosynthesis rates by allowing plants to more efficiently use water, because they no longer need to leave their stomata open for such long periods of time in order to absorb the same amount of carbon dioxide.
- Humans also affect the oceanic carbon cycle.
  - Higher ocean temperatures modify ecosystems.
  - Acid rain and polluted runoff from agriculture and industry affect ecosystems, such as coral reefs, limiting the ocean's ability to absorb carbon from the atmosphere on a regional scale and reducing oceanic biodiversity globally.

http://en.wikipedia.org/wiki/Carbon_cycle

Human Influence



Units are in gigatons.

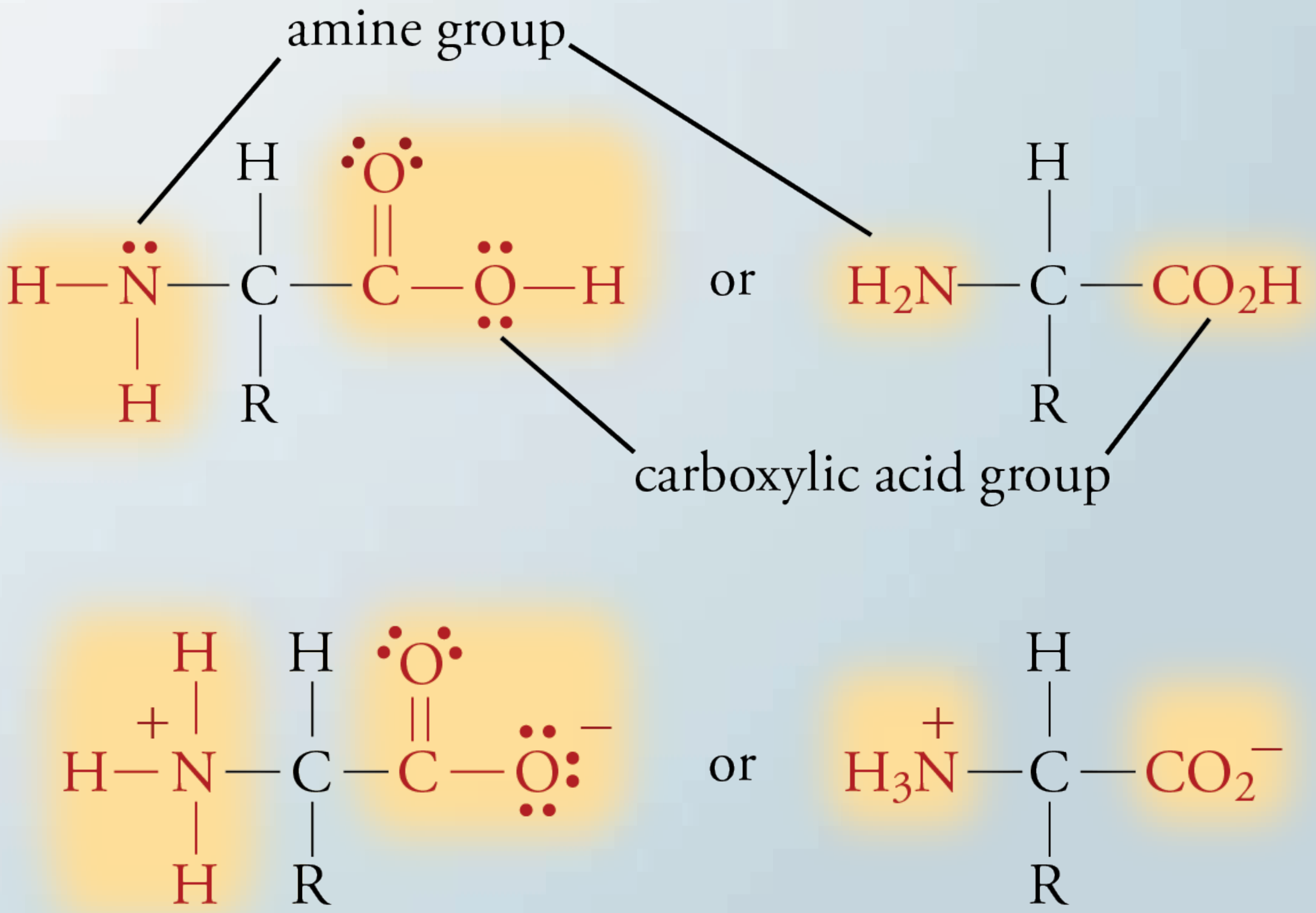
http://en.wikipedia.org/wiki/Carbon_cycle

Nitrogen Cycle

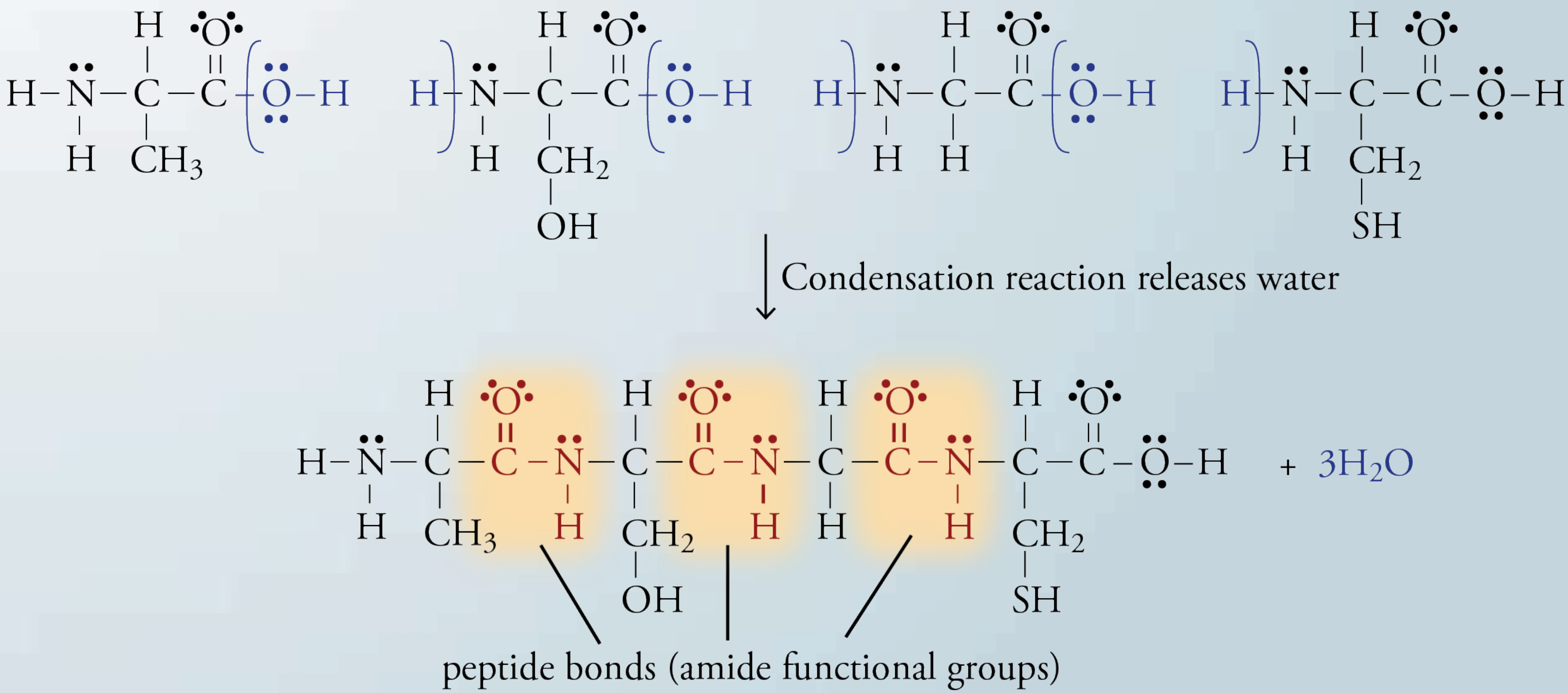
- The **nitrogen cycle** is the process by which nitrogen is converted among its various chemical forms.
- The majority of Earth's atmosphere (approximately 78%) is nitrogen, making it the largest pool of nitrogen.
- Atmospheric nitrogen has limited availability for biological use, leading to a scarcity of usable nitrogen in many types of ecosystems.
- Important processes in the nitrogen cycle include fixation, nitrification, and denitrification.

Nitrogen in Amino Acids and Proteins

- Nitrogen is in all amino acids, which form proteins.



Formation of Ala-Ser-Gly-Cys

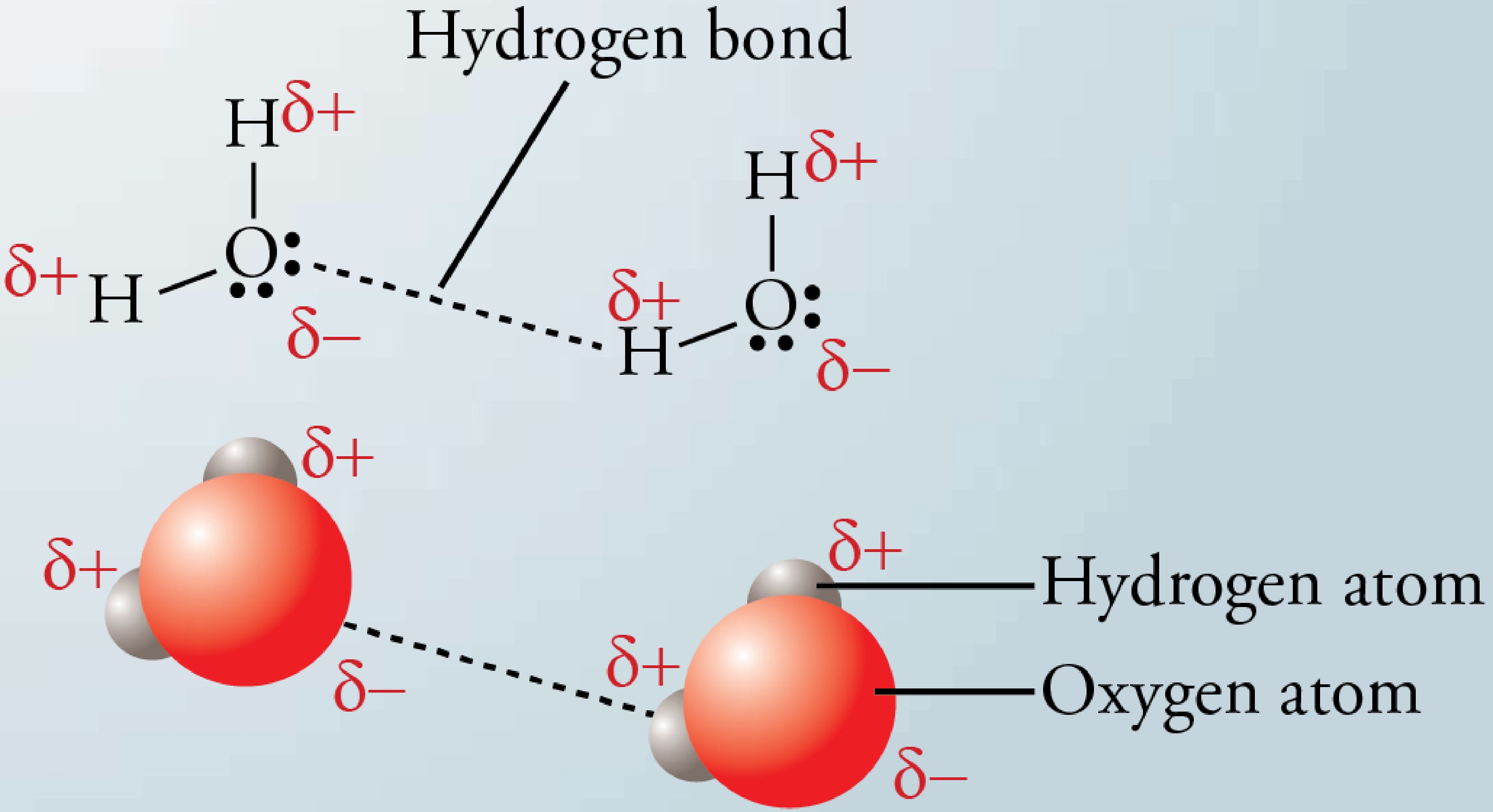


Primary and Secondary Protein Structures

- ***Primary Structure*** = the sequence of amino acids in the protein
- The arrangement of atoms that are close to each other in the polypeptide chain is called the ***secondary structure*** of protein.
  - Three types
    - α-helix
    - β-sheet
    - irregular

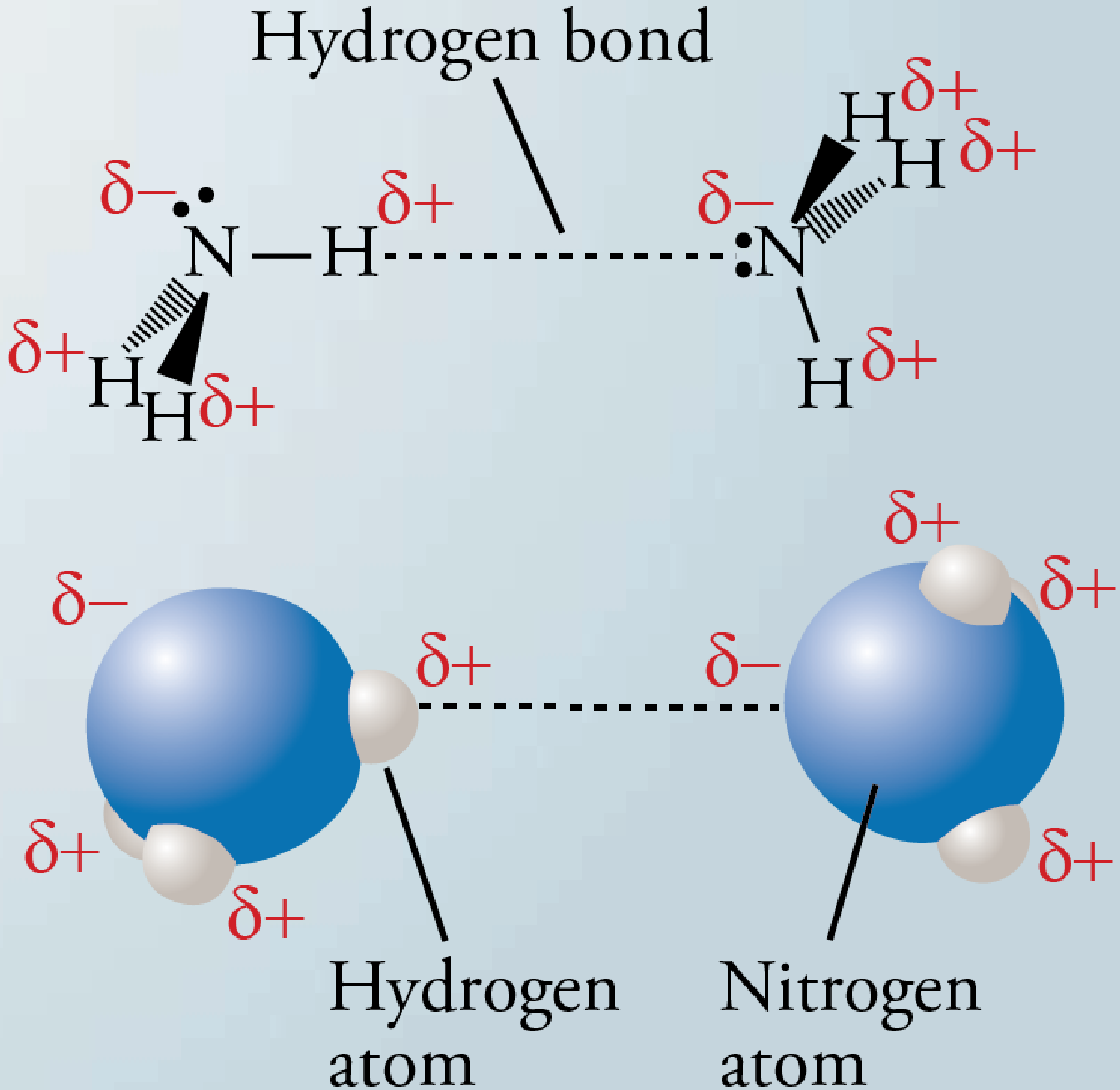
Hydrogen Bonds in Water

In H_2O, the hydrogen bond is between the partial positive H of one H_2O molecule and the partial negative O of another H_2O molecule.

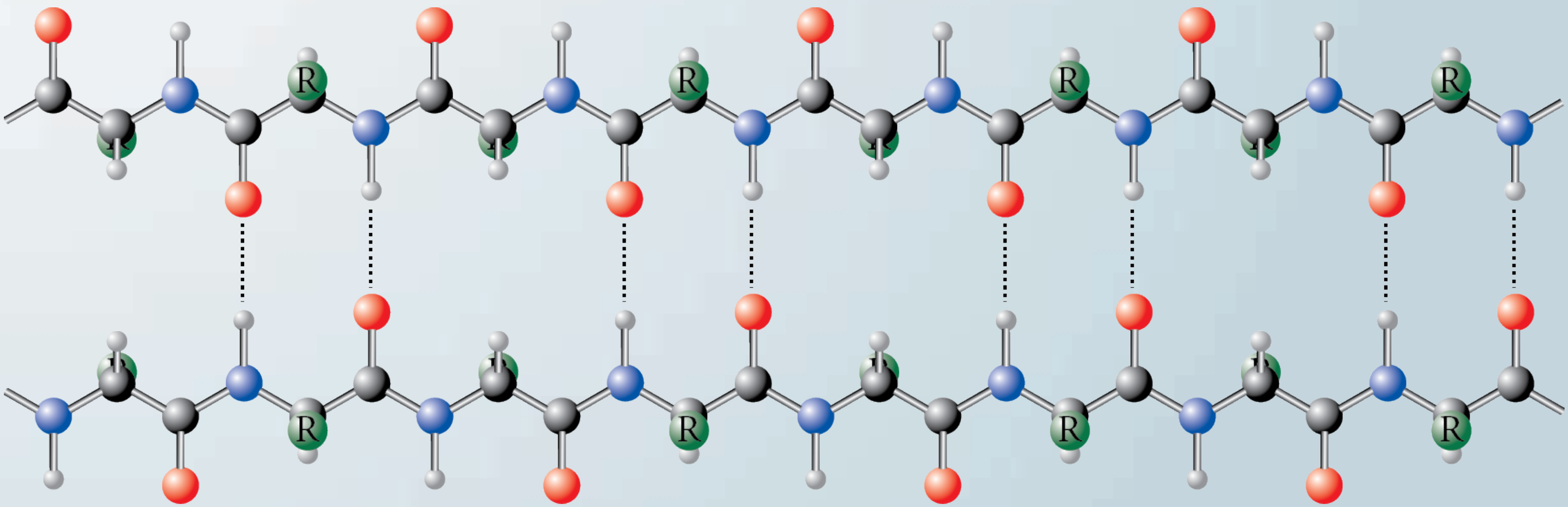


Hydrogen Bonds in Ammonia

In NH_3, the hydrogen bond is between the partial positive H of one NH_3 molecule and the partial negative N of another NH_3 molecule.

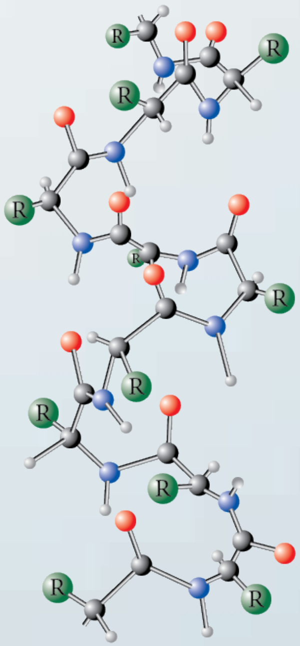


β-Sheet Secondary Structure

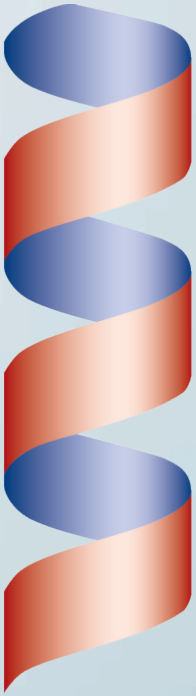


α-helix - Secondary Structure

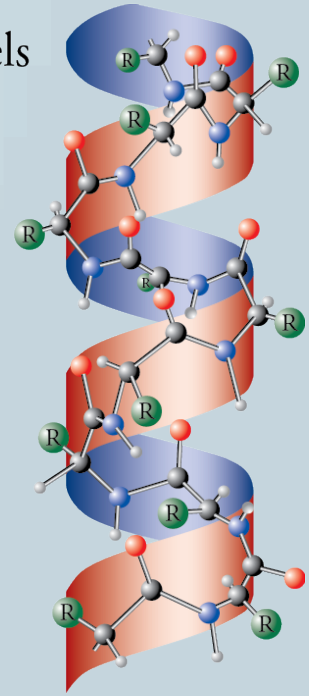
Ball-and-stick model of a portion of the α-helical secondary structure of a protein molecule



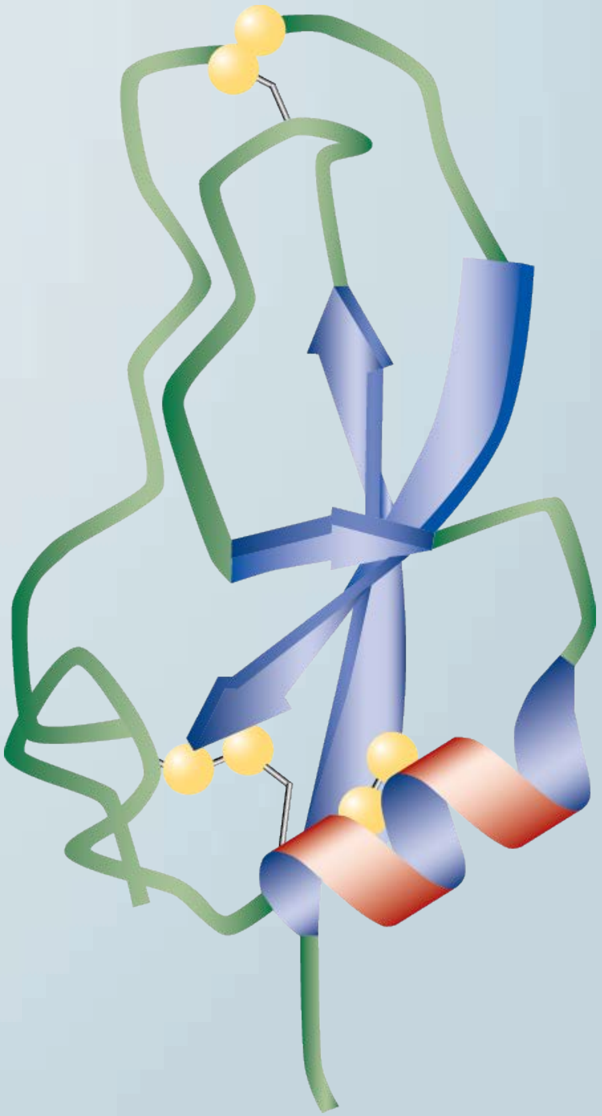
This ribbon model shows the general arrangement of atoms in a portion of the α-helical secondary structure of a protein molecule.



The two models superimposed



Protein - Bovine Pancreatic Trypsin Inhibitor (BPTI)

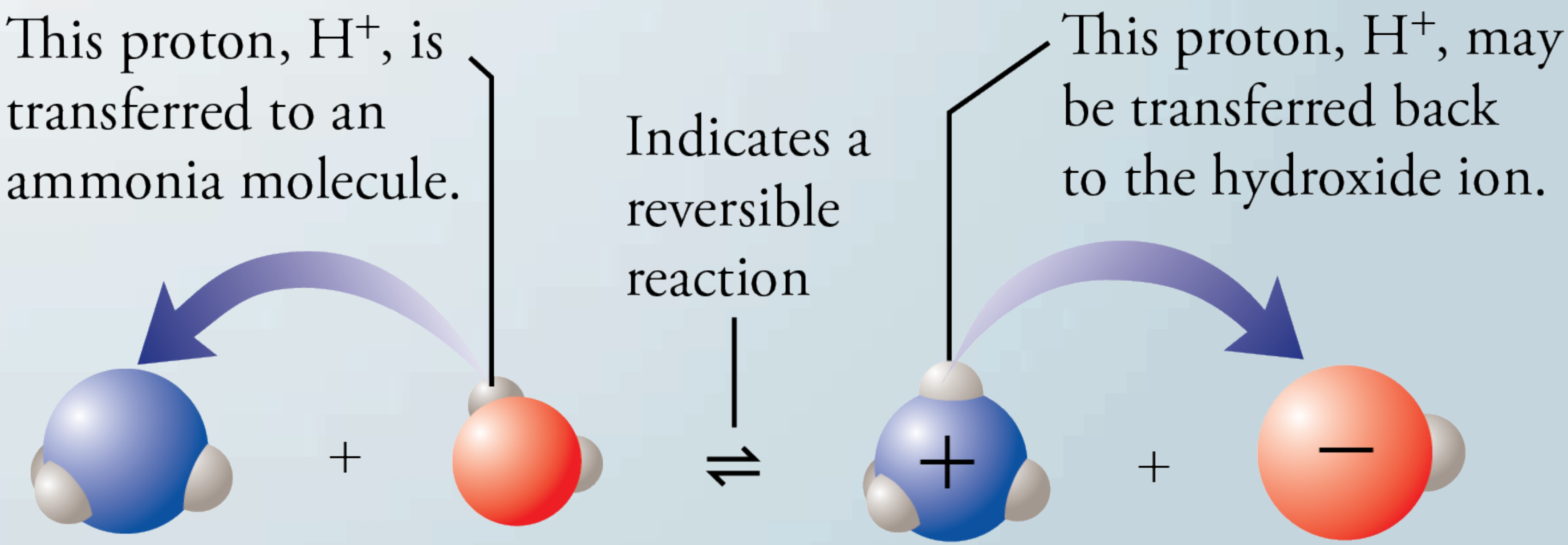


Nucleic Acids

- Nitrogen is an important element in nucleobases that make up nucleic acids, such as DNA and RNA.
- Nucleic acids encode and transmit genetic information.
- They include DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).
- Nucleic acids were named for their initial discovery within the cell nucleus, and for the presence of phosphate groups (related to phosphoric acid).
- Found in all life forms.
- All living cells and organelles contain both DNA and RNA, while viruses contain either DNA or RNA, but usually not both.

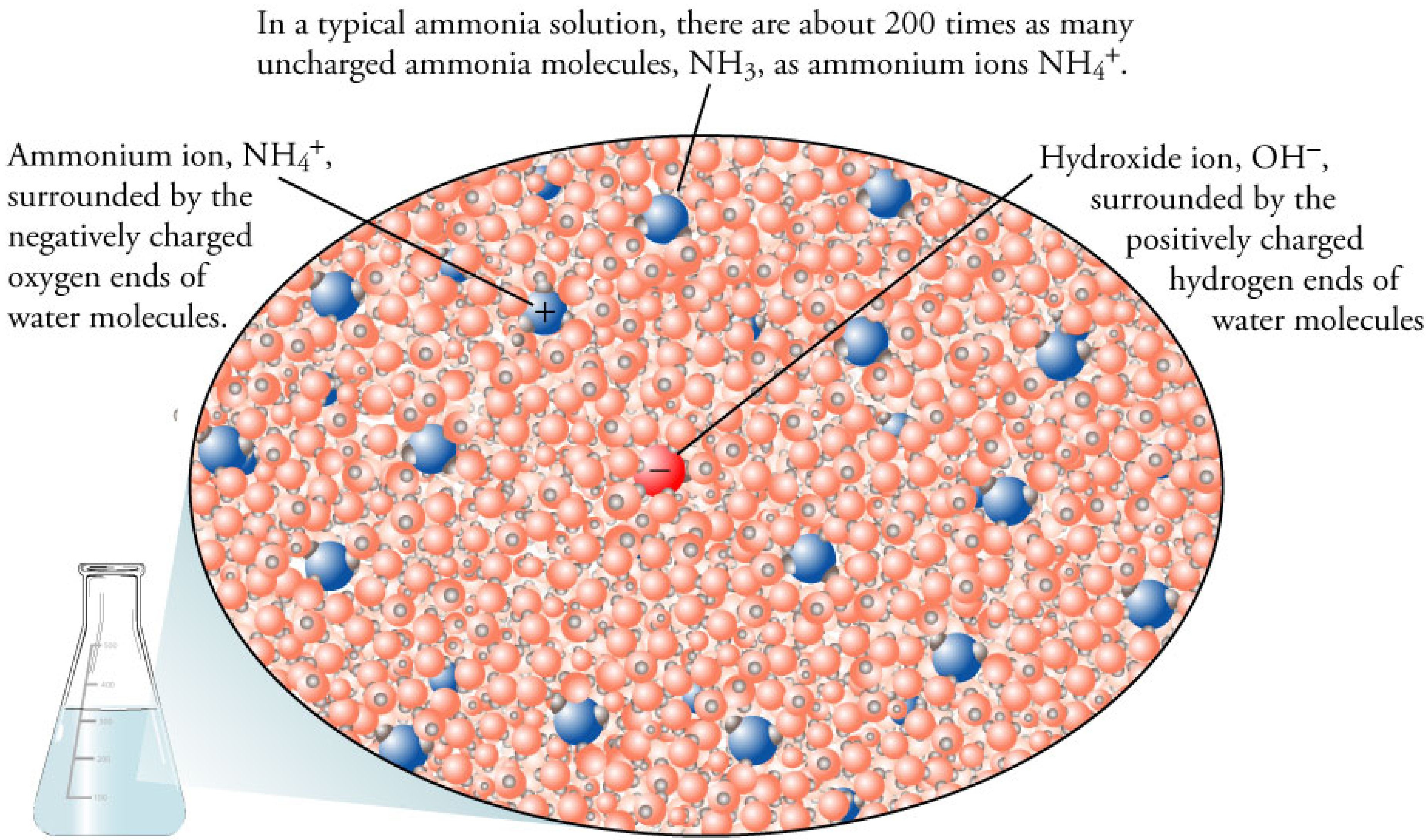
Ammonia and Water

Ammonia reacts with water in a reversible reaction, which forms ammonium and hydroxide ions.



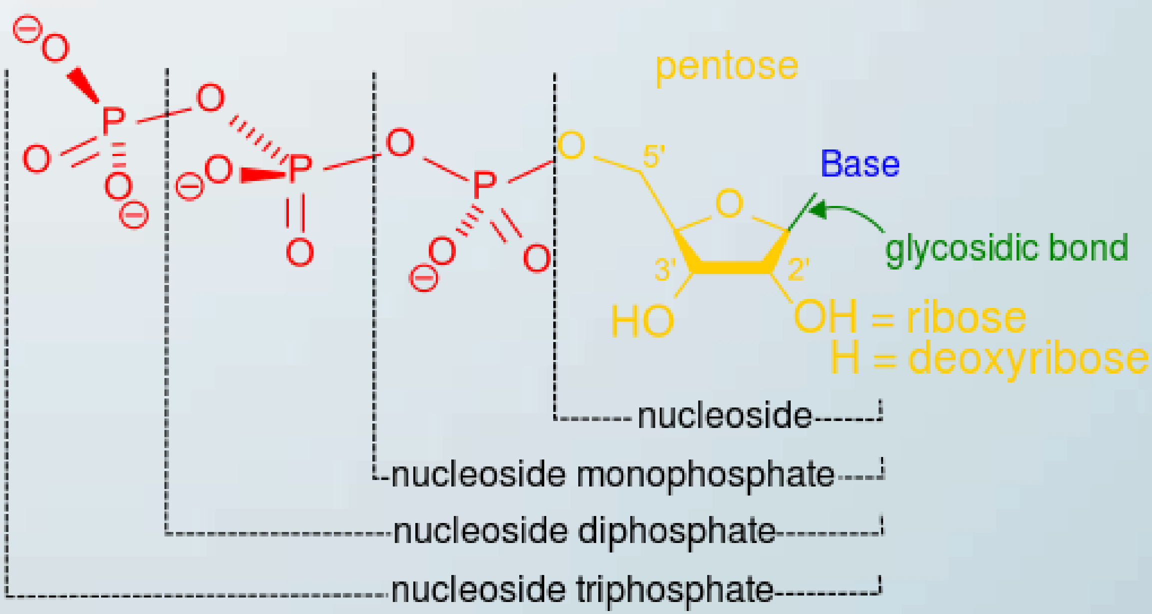
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

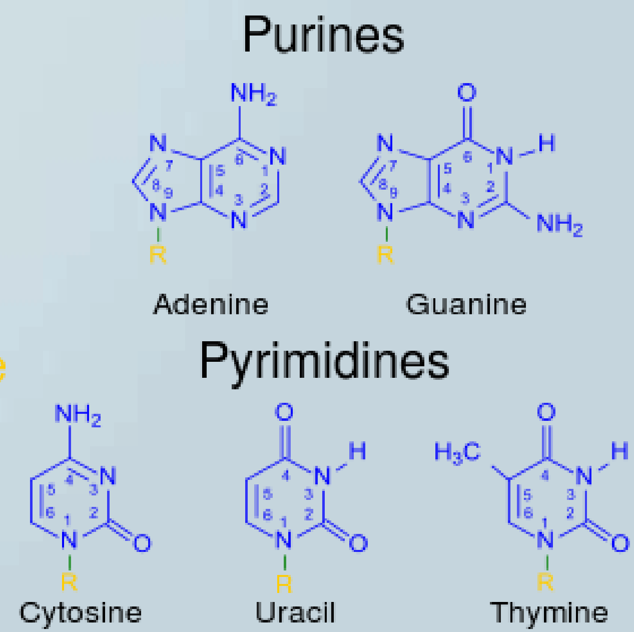
Ammonia Solution



Nucleotides

- Nucleic acids are polymers of repeating nucleotides, each of which contains a pentose sugar (ribose or deoxyribose), a phosphate group, and a nucleobase.

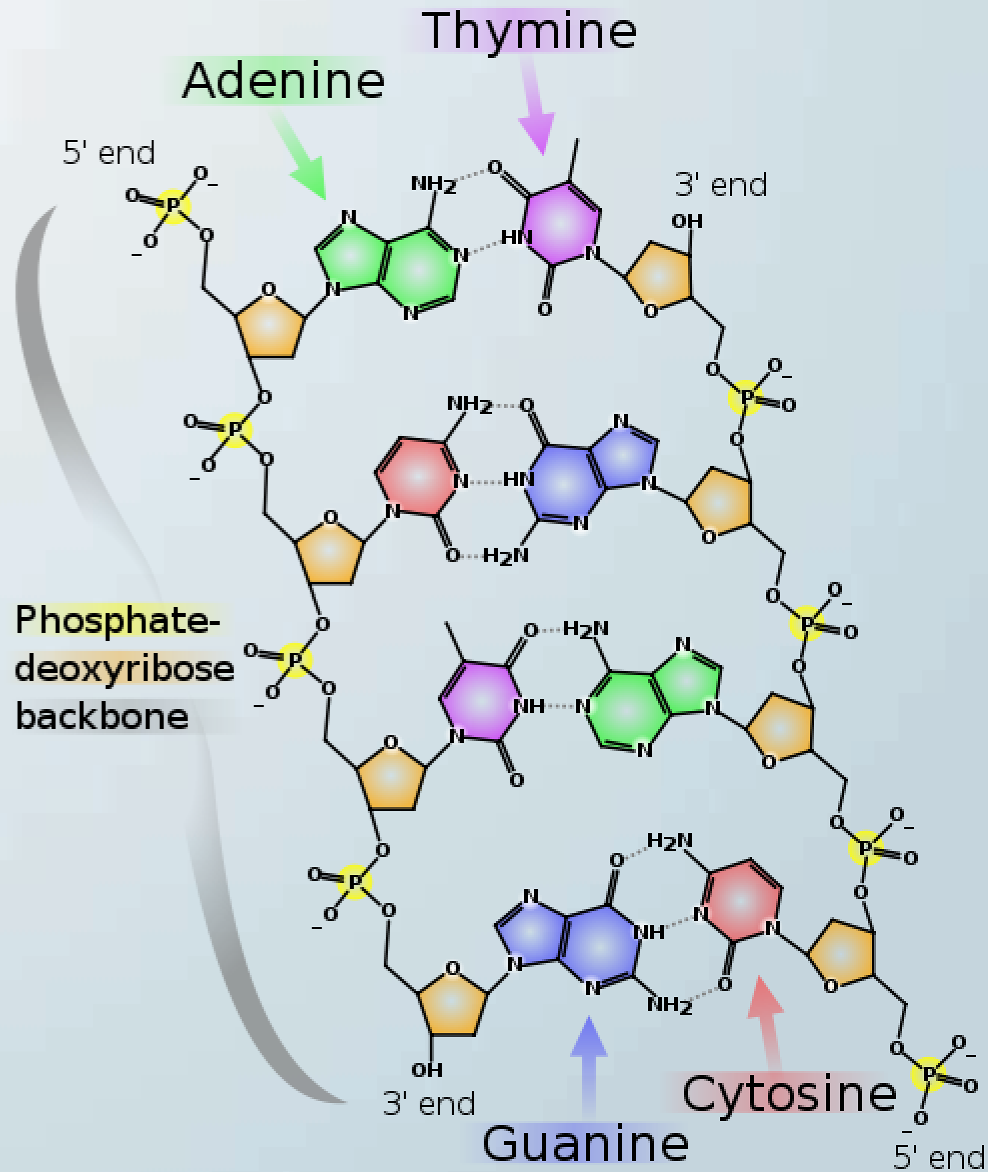




DNA, Deoxyribonucleic Acid

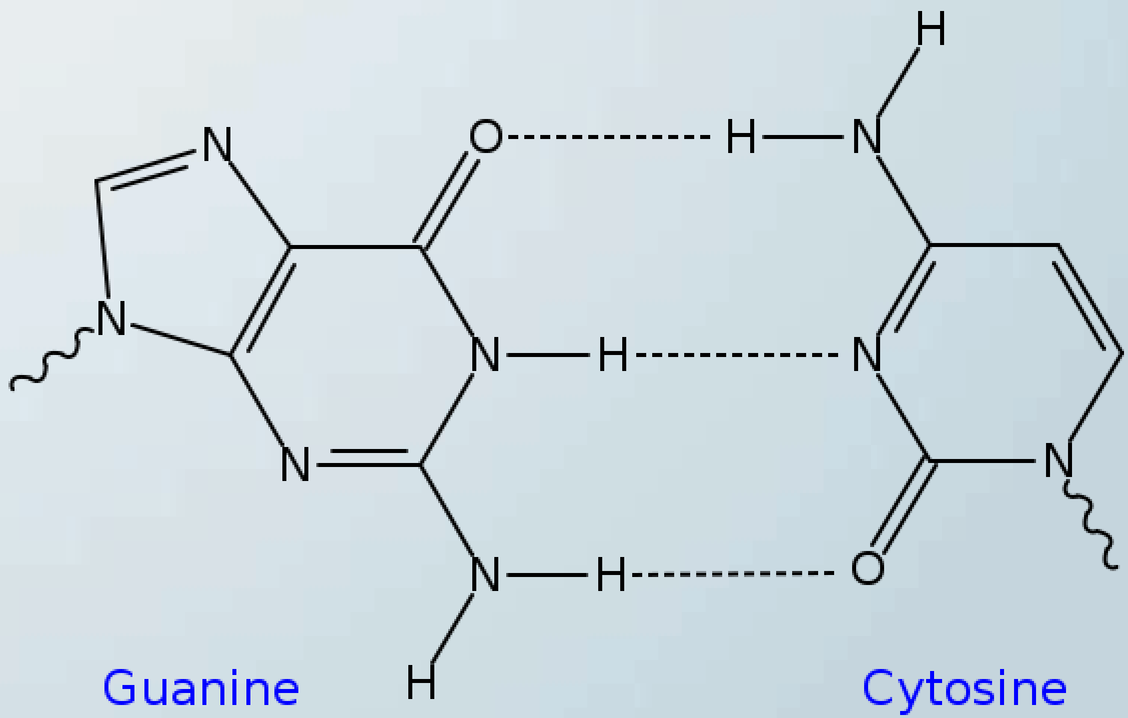
- **Deoxyribonucleic acid** (**DNA**) is a nucleic acid containing the genetic instructions used in the development and functioning of all known living organisms (with the exception of RNA viruses).
- The DNA segments carrying this genetic information are called genes.
- Double helix - two long polymers of repeating nucleotides.
- Backbones made of sugars and phosphate groups.
- Attached to each sugar is one of four types of molecules called nucleobases (informally called *bases*).
- Sequence of these four nucleobases encodes information and specifies the sequence of the amino acids linked together to form proteins.

DNA


Thymine
Adenine
5' end
3' end
Phosphate-
deoxyribose
backbone
3' end
5' end
Guanine
Cytosine

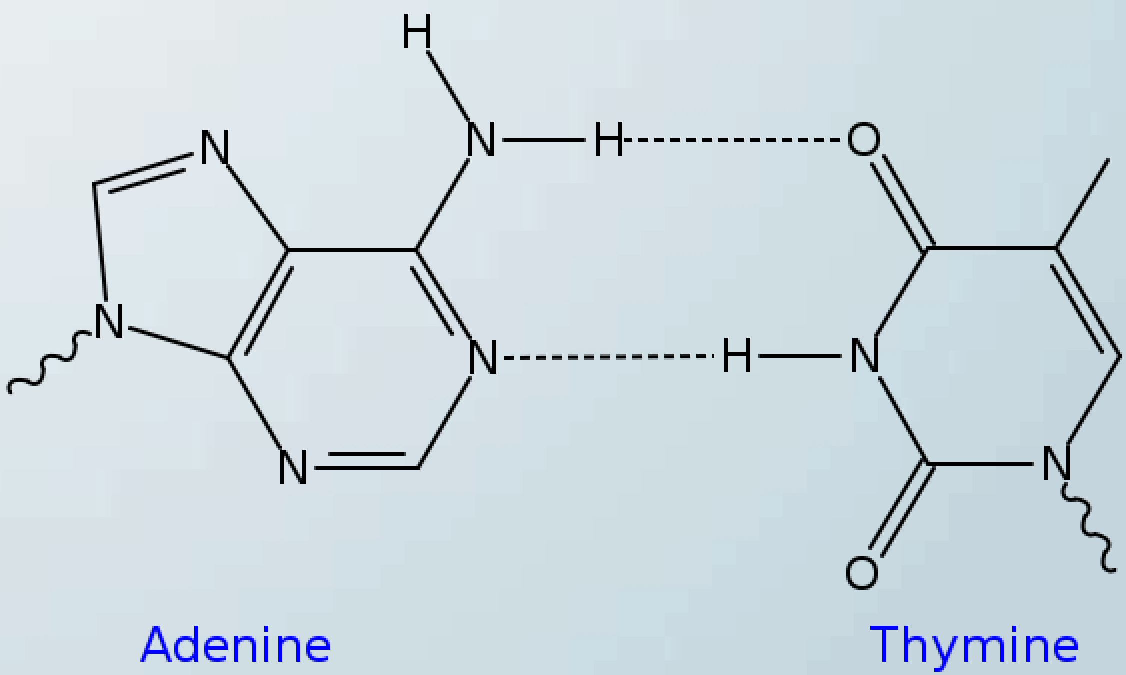
Base Pairing

- The guanine nucleobase links to the cytosine nucleobase by hydrogen bonds.

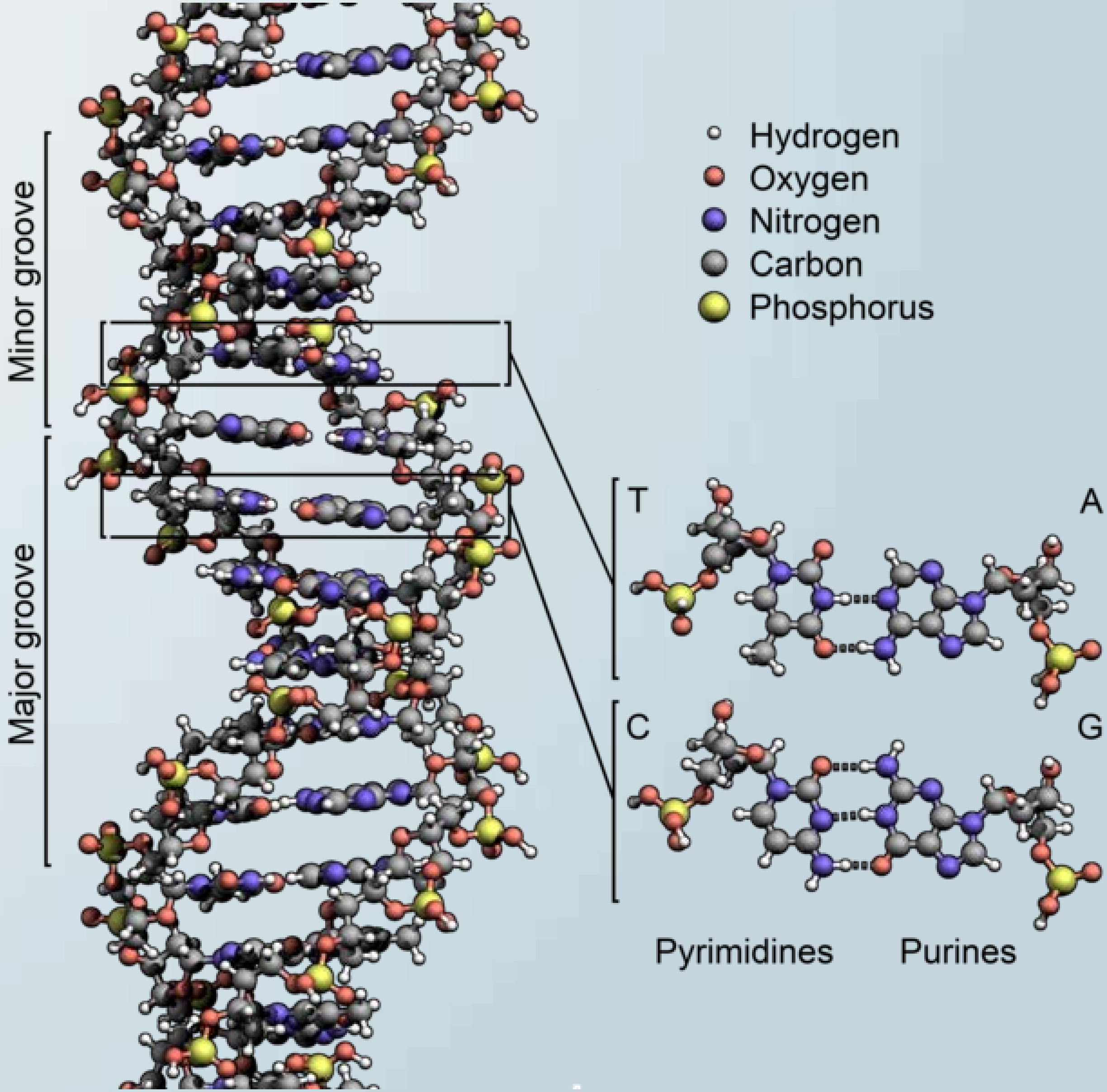


Base Pairing

- The adenine nucleobase links to the thymine nucleobase by hydrogen bonds.



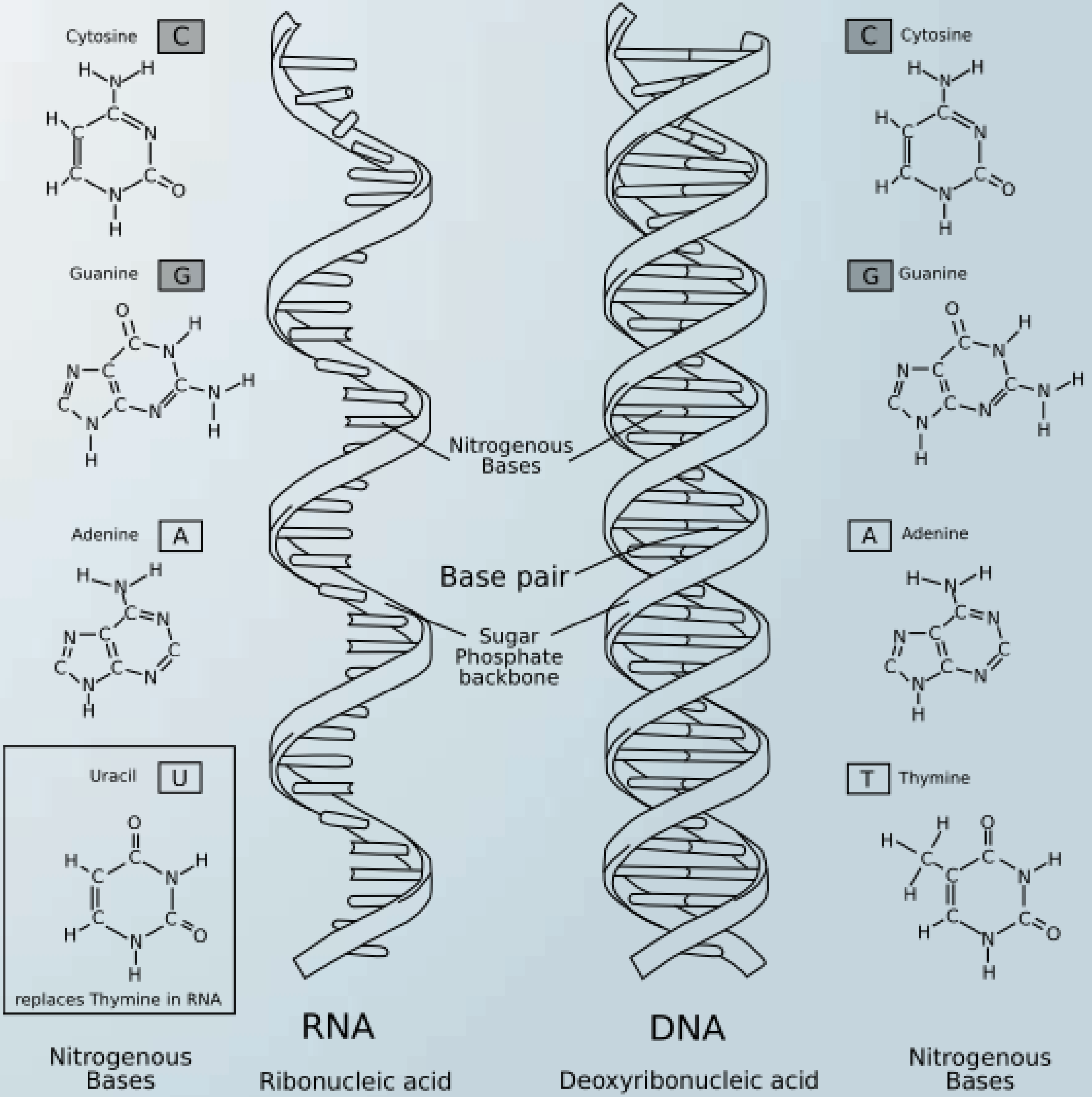
DNA Double Helix



RNA, Ribonucleic Acid

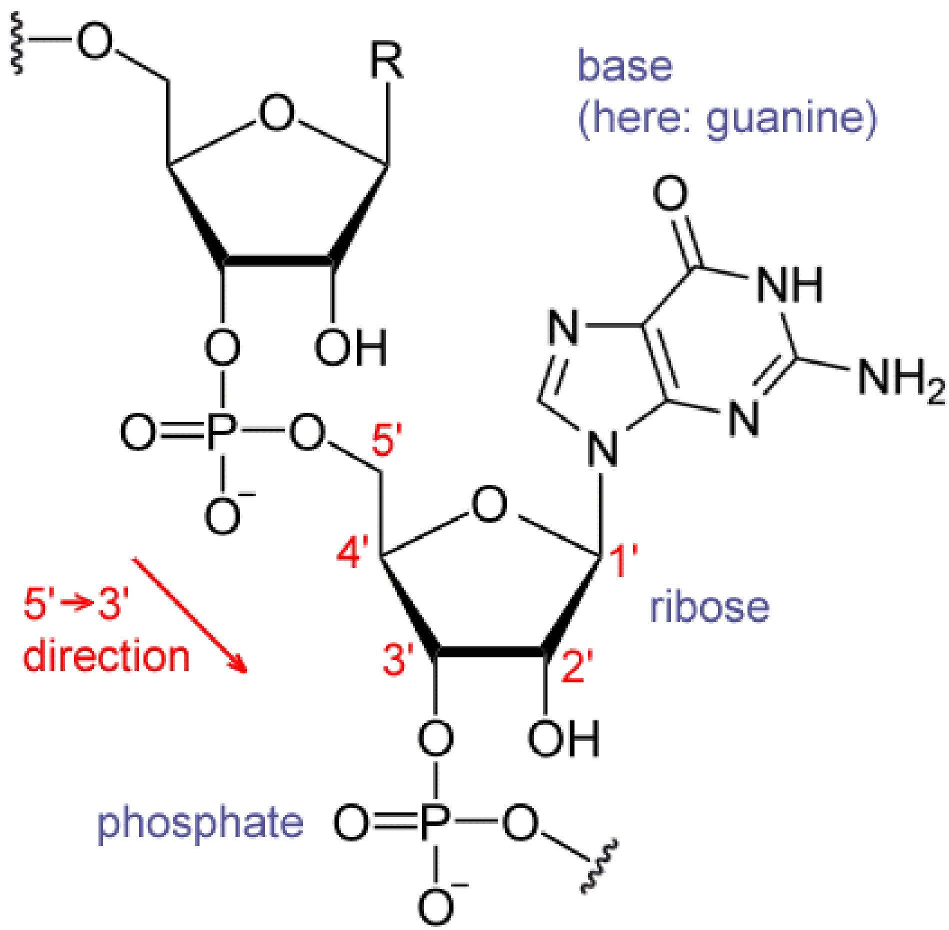
- All cellular organisms use messenger RNA (mRNA) to carry the genetic information that directs the synthesis of proteins.
- Many viruses use RNA instead of DNA as their genetic material.
- Transfer RNA (tRNA) molecules to deliver amino acids to the ribosome, where ribosomal RNA (rRNA) links amino acids together to form proteins.
- Differences from DNA
  - RNA contains the sugar *ribose*, while DNA contains the slightly different sugar *deoxyribose* (a type of ribose that lacks one oxygen atom
  - RNA has the nucleobase uracil while DNA contains thymine.
  - Unlike DNA, most RNA molecules are single-stranded and can adopt very complex three-dimensional structures.

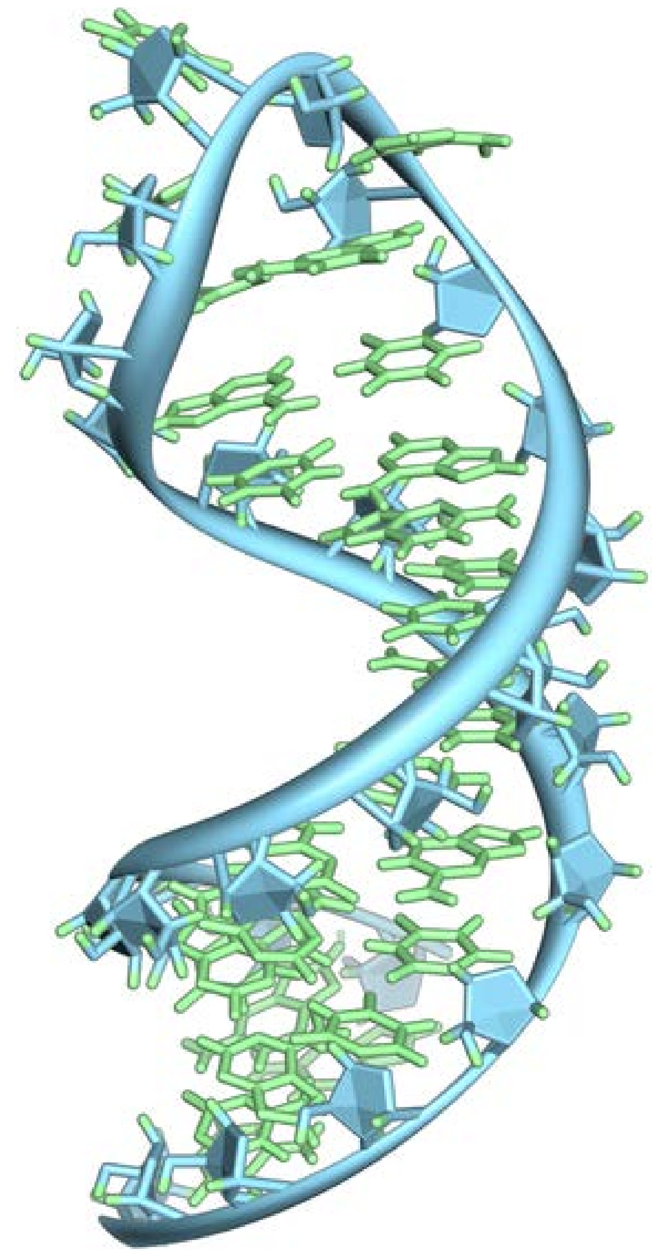
DNA and RNA



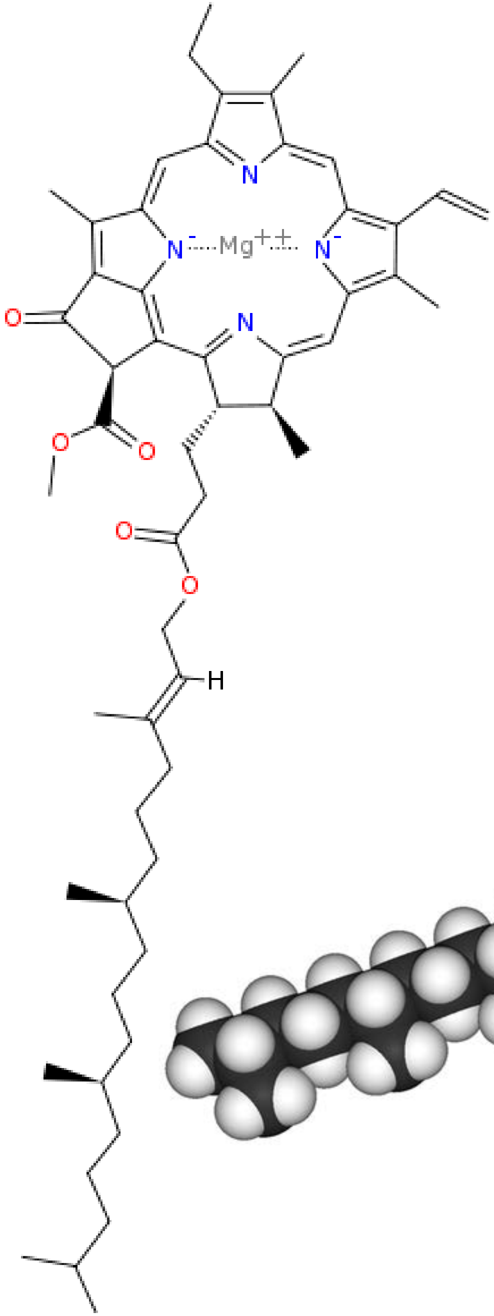
Cytosine
C
Guanine
G
Adenine
A
Uracil
U
replaces Thymine in RNA
Nitrogenous Bases
Base pair
Sugar Phosphate backbone
RNA
Ribonucleic acid
DNA
Deoxyribonucleic acid
Thymine
T
Nitrogenous Bases

RNA

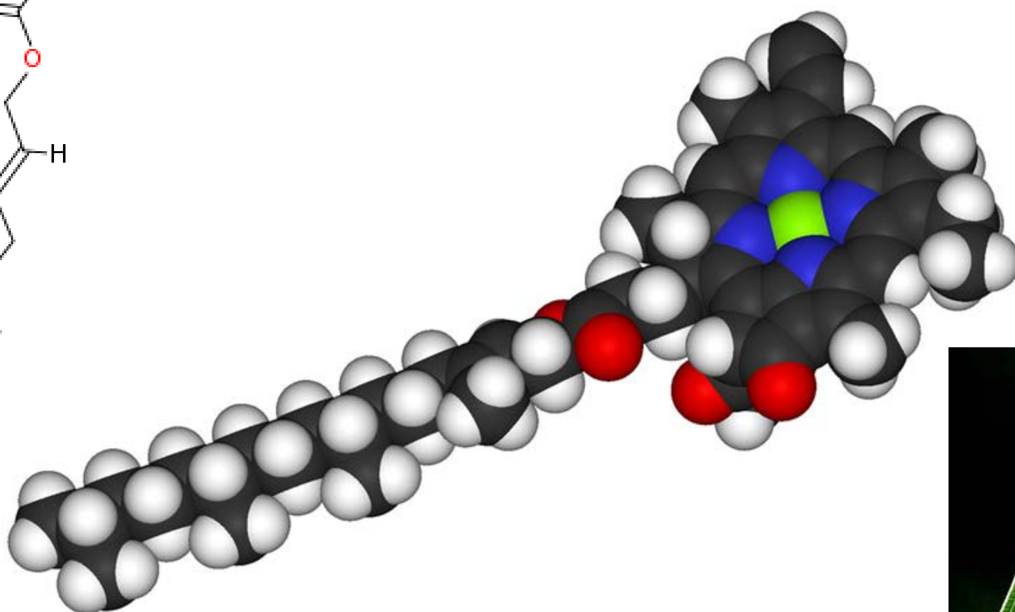




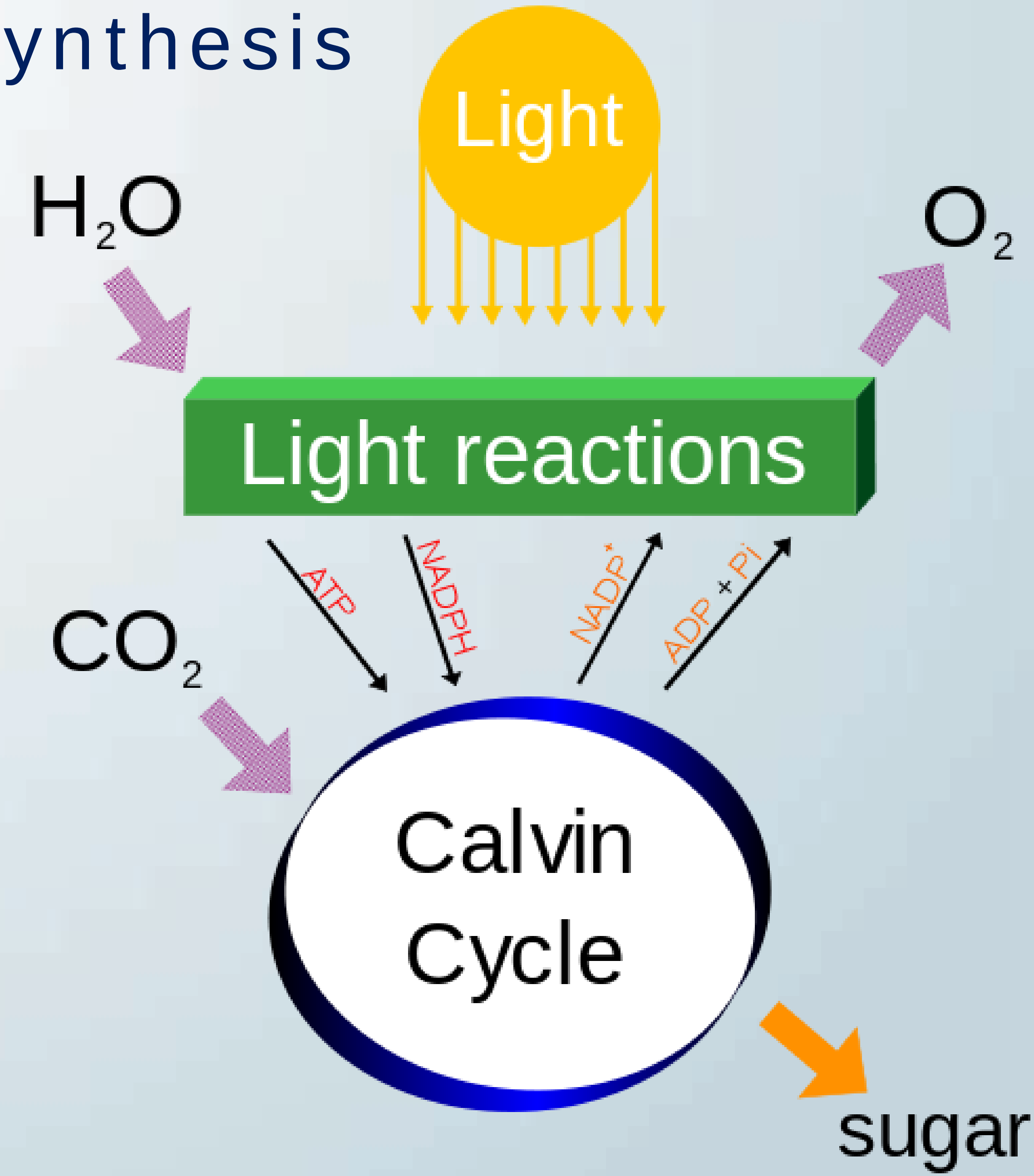
Chlorophyll



- In plants, much of the nitrogen is used in chlorophyll molecules, which are essential for photosynthesis and further growth.
- Chlorophyll is a green pigment that allows plants to absorb energy from light.



Photosynthesis



Nitrogen Cycle Issues

- The abundance or scarcity of the "fixed" form of nitrogen, (also known as reactive nitrogen), dictates how much food can be grown on a piece of land.
- Nitrogen availability can affect the rate of key ecosystem processes, including primary production and decomposition.
- Human activities such as fossil fuel combustion, use of artificial nitrogen fertilizers, and release of nitrogen in wastewater have dramatically altered the global nitrogen cycle.

Chemical Forms of Nitrogen

N_2	Nitrogen gas	78% of atmosphere; most of N
NH_3	Ammonia	nutrient form
NH_4^+	Ammonium ion	nutrient form
NO_2^-	Nitrite ion	
NO_3^-	Nitrate ion	Principle nutrient form; very soluble
$-NH_{(2)}$	Amino group	In amino acids and proteins
N_2O	Nitrous oxide	Controls ozone cycle
NO	Nitrogen monoxide	Combustion product
NO_2	Nitrogen dioxide	Oxidized NO; acid precursor
NH_4NO_3	Ammonium nitrate	fertilizer

Nitrogen Fixation

- **Nitrogen fixation** is a process by which nitrogen (N_2) in the atmosphere is converted into ammonia (NH_3).
  - Atmospheric nitrogen or elemental nitrogen (N_2) is relatively inert: it does not easily react easily with other chemicals to form new compounds.
  - Fixation processes free up the nitrogen atoms from their diatomic form (N_2) to be used in other ways.

http://en.wikipedia.org/wiki/Nitrogen_fixation

Ways to Fix Nitrogen

- Biological fixation (more to come)
- Industrial N-fixation: Haber-Bosch process which is used to make fertilizer and explosives

  $N_2 + 3H_2 \rightleftharpoons 2NH_3$

  This conversion is typically conducted at 15–25 MPa (150–250 bar) and between 300 and 550 °C
- Combustion of fossil fuels: automobile engines and thermal power plants, which release various nitrogen oxides (NO_x).
- Other processes: The energy derived from photons and lightning can fix nitrogen, forming NO from N_2 and O_2.

Biological Nitrogen Fixation

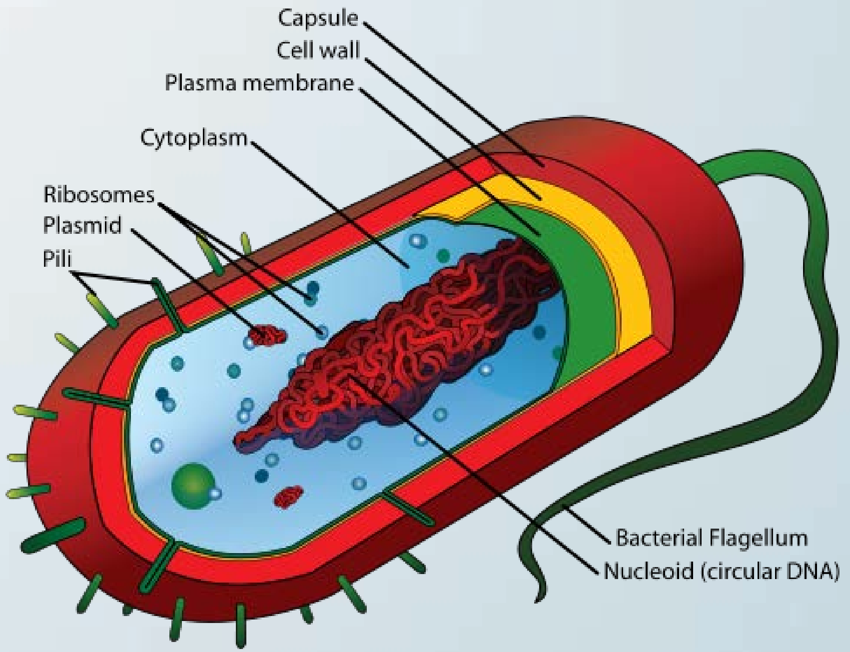
- Biological nitrogen fixation (BNF) occurs when atmospheric nitrogen is converted by diazotrophs to ammonia. The reaction for BNF is:

$$N_2 + 8\,H^+ + 8\,e^- \rightarrow 2\,NH_3 + H_2$$

  - **Diazotrophs** = bacteria and single-cell microorganisms that fix atmospheric nitrogen gas into a more usable form such as ammonia.

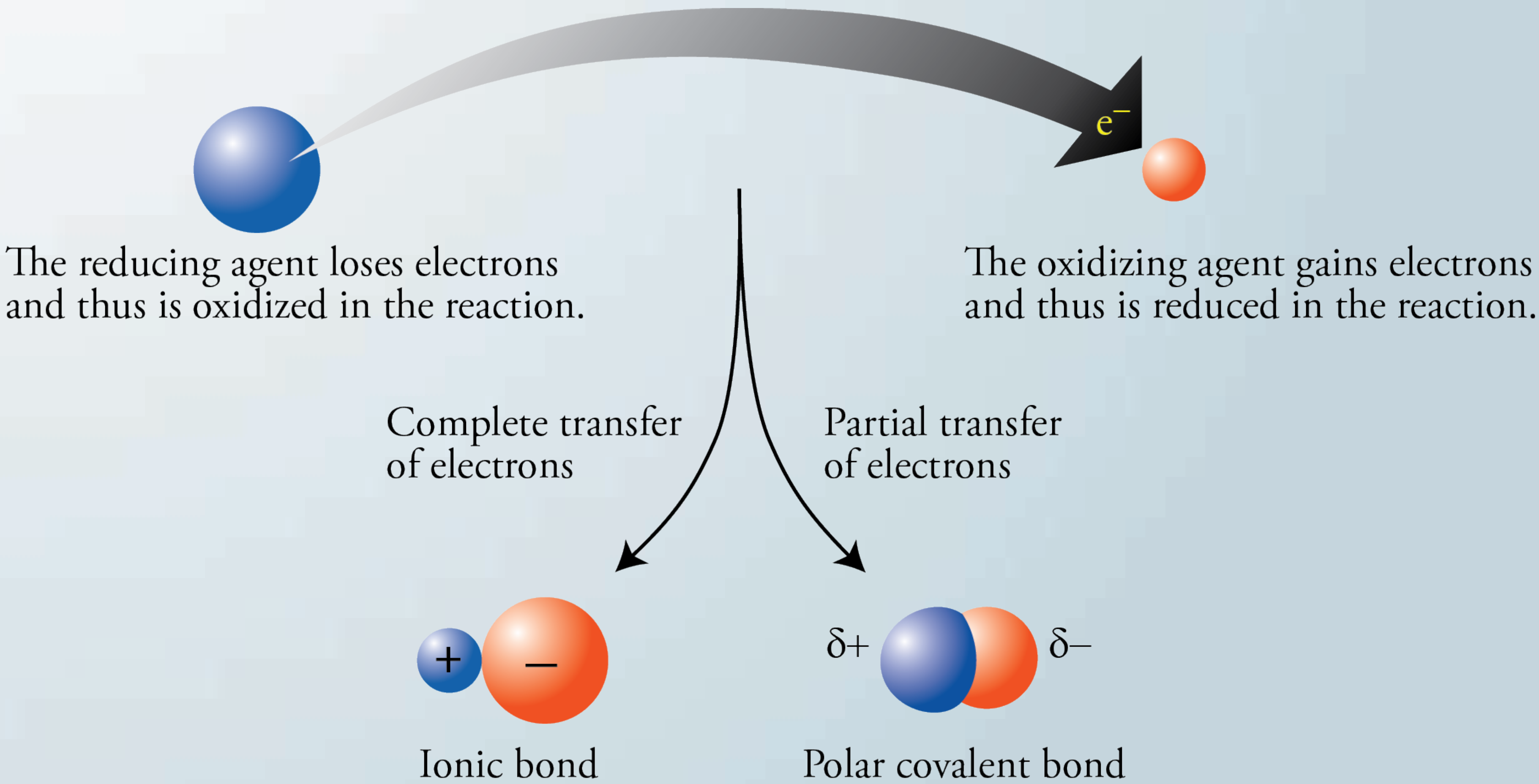
Bacteria

- Prokaryotic microorganisms (Prokaryotes lack a cell nucleus or any other membrane-bound organelles.)



- About 40 million bacterial cells in a gram of soil
- About a million bacterial cells per mL fresh water
- Approximately five nonillion (5×10^{30}) bacteria on Earth
- Biomass greater than all plants and animals.

Oxidation-Reduction (Redox)



Redox Terms

- **Oxidation-Reduction (Redox) Reaction**
  - an electron transfer reaction
- **Oxidation**
  - complete or partial loss of electrons
- **Reduction**
  - complete or partial gain of electrons
- **Oxidizing Agent**
  - the substance reduced; gains electrons, making it possible for something to lose them.
- **Reducing Agent**
  - the substance oxidized; loses electrons, making it possible for something to gain them.

Questions Answered by Oxidation Numbers

Is the reaction redox?	If any atoms change their oxidation number, yes.
What's oxidized?	The element that increases its oxidation number
What's reduced?	The element that decreases its oxidation number
What's the reducing agent?	The substance with the element oxidized
What's the oxidizing agent?	The substance with the element reduced

Steps for Determination of Oxidation Numbers

- **Step 1:** Assign oxidation numbers to as many atoms as you can using the guidelines described on the next slide.
- **Step 2:** To determine oxidation numbers for atoms not described on the pervious slide, use the following guideline.
  - The sum of the oxidation numbers for each atom in the formula is equal to the overall charge on the formula. (This includes uncharged formulas where the sum of the oxidation numbers is zero.)

$N_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ NH_3 + H_2$

N changes from 0 to +3 so oxidized,

N_2 reducing agent

H changes from +1 to 0 so reduced

H_2 oxidizing agent

Oxidation Numbers

uncharged element	0	no exceptions
monatomic ions	charge on ion	no exceptions
combined fluorine	-1	no exceptions
combined oxygen	-2	-1 in peroxides
covalently bonded hydrogen	+1	no exceptions

Plant Role in Nitrogen Fixation

- Plants that contribute to nitrogen fixation include the legume family – kudzu, clovers, soybeans, alfalfa, lupines, peanuts, and rooibos.
  - A **legume** is (1) a pod, such as that of a pea or bean, that splits into two valves with the seeds attached to one edge of the valves or (2) a plant that has such a pod.
- They contain symbiotic bacteria called *Rhizobia* within nodules in their root systems, producing nitrogen compounds that help the plant to grow and compete with other plants.

Nitrification

- Ammonium is converted to nitrate primarily by bacteria.
- Certain bacteria oxidize ammonium (NH_4^+), converting it to nitrites (NO_2^-).

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

- Other bacterial species oxidize the nitrites into nitrates (NO_3^-). It is important for the nitrites to be converted to nitrates because accumulated nitrites are toxic to plant life.

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

- Plants can absorb nitrate or ammonium ions from the soil through their roots. If nitrate is absorbed, it is first reduced to nitrite ions and then ammonium ions for incorporation into amino acids, nucleic acids, and chlorophyll.

Plant Role in Nitrogen Fixation

- When the plant dies, the fixed nitrogen is released, making it available to other plants and this helps to fertilize the soil.
- In many traditional and organic farming practices, fields are rotated through various types of crops, which usually includes one consisting mainly or entirely of clover or buckwheat, which are often referred to as "green manure".

http://en.wikipedia.org/wiki/Nitrogen_fixation

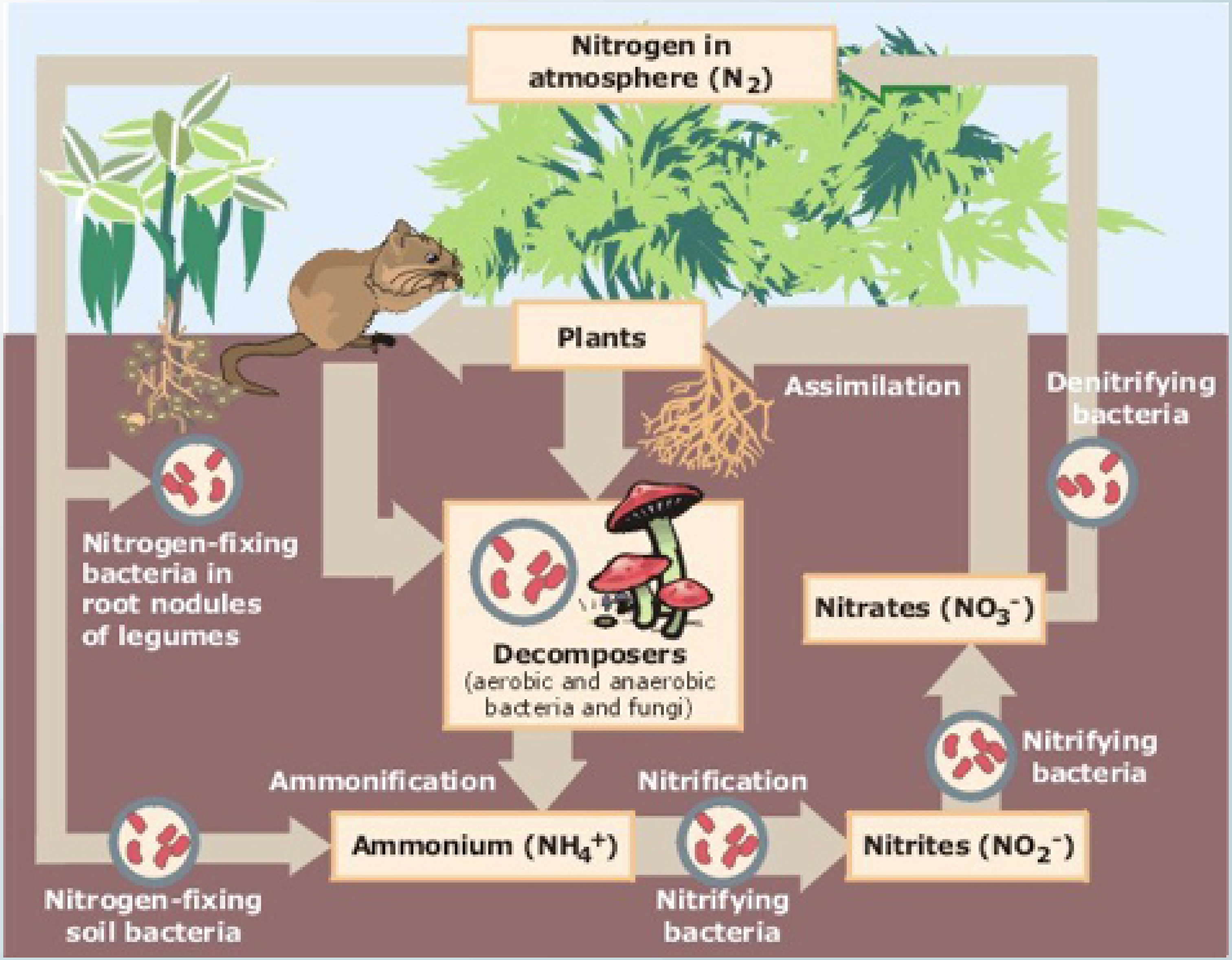
Denitrification

Denitrification = conversion (by bacteria) of nitrate into non-reactive atmospheric nitrogen gases N_2 and N_2O

$$4NO_3^- + 2H_2O \rightarrow 2N_2 + 5O_2 + 4OH^-$$

$$C_6H_{12}O_6 + 6NO_3^- \rightarrow 6CO_2 + 3H_2O + 6OH^- + 3N_2O$$

Nitrogen Cycle



Problems Associated with Nitrates

- Nitrates can enter groundwater.
- Elevated nitrate in groundwater is a concern for drinking water use because nitrate can interfere with blood-oxygen levels in infants and cause methemoglobinemia or blue-baby syndrome.
- Nitrate-enriched groundwater can contribute to eutrophication, a process that leads to high algal, especially blue-green algal populations.
- Since 2006, the application of nitrogen fertilizer has been increasingly controlled in Britain and the United States.

http://en.wikipedia.org/wiki/Nitrogen_fixation

Human Effects on Nitrogen Cycle

- Humans have more than doubled the annual transfer of nitrogen into biologically-available forms due to
  - extensive cultivation of legumes (particularly soy, alfalfa, and clover),
  - growing use of the Haber-Bosch process in the creation of chemical fertilizers,
  - pollution emitted by vehicles and industrial plants
- In addition, humans have significantly contributed to the transfer of nitrogen trace gases to the atmosphere, and from the land to aquatic systems.
- Human alterations to the global nitrogen cycle are most intense in developed countries and in Asia, where vehicle emissions and industrial agriculture are highest.

http://en.wikipedia.org/wiki/Nitrogen_fixation

Human Effects on Nitrogen Cycle

- Nitrous oxide (N_2O), which is a greenhouse gas and which, has risen in the atmosphere as a result of agricultural fertilization, biomass burning, cattle and feedlots, and industrial sources.
  - Greenhouse gas - currently the third largest contributor to global warming, after carbon dioxide and methane.
  - Contributes to the destruction of stratospheric ozone
- Ammonia (NH_3) in the atmosphere has tripled as the result of human activities.
  - Eventually yields nitric acid that contributes to acid rain.
  - Atmospheric ammonia and nitric acid damage respiratory systems.

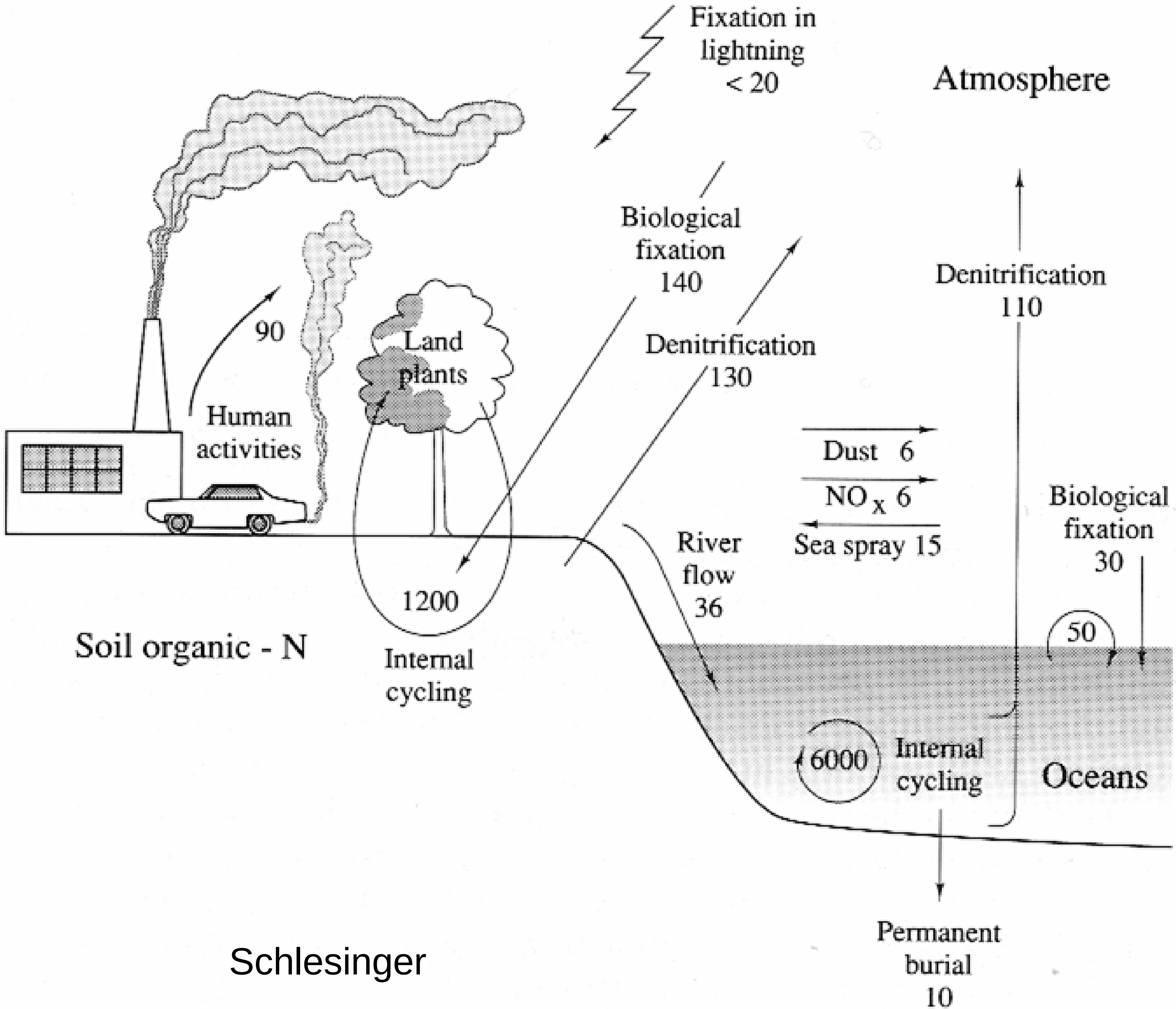
http://en.wikipedia.org/wiki/Nitrogen_fixation

Human Effects on Nitrogen Cycle

- All forms of high-temperature combustion have contributed to a 6 or 7 fold increase in the flux of NO_x to the atmosphere.
- Ammonia and nitrous oxides contribute to the formation of tropospheric (lower atmosphere) ozone production.
- Decreases in biodiversity can also result if higher nitrogen availability increases nitrogen-demanding grasses.

http://en.wikipedia.org/wiki/Nitrogen_fixation

Global N Cycle TgN, TgN/y



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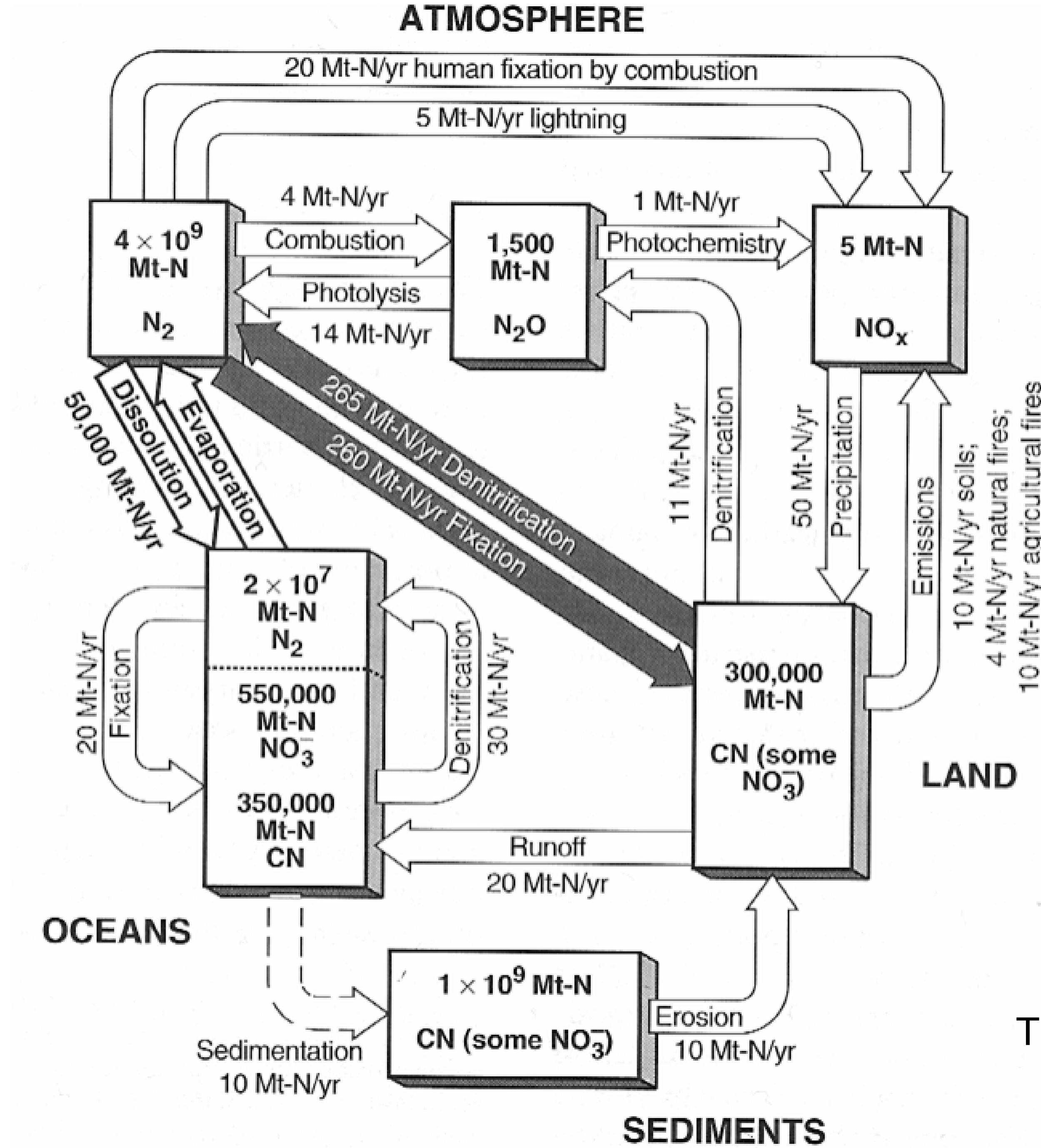
Global N Cycle Stocks and Flows



Turco

Sulfur Cycle

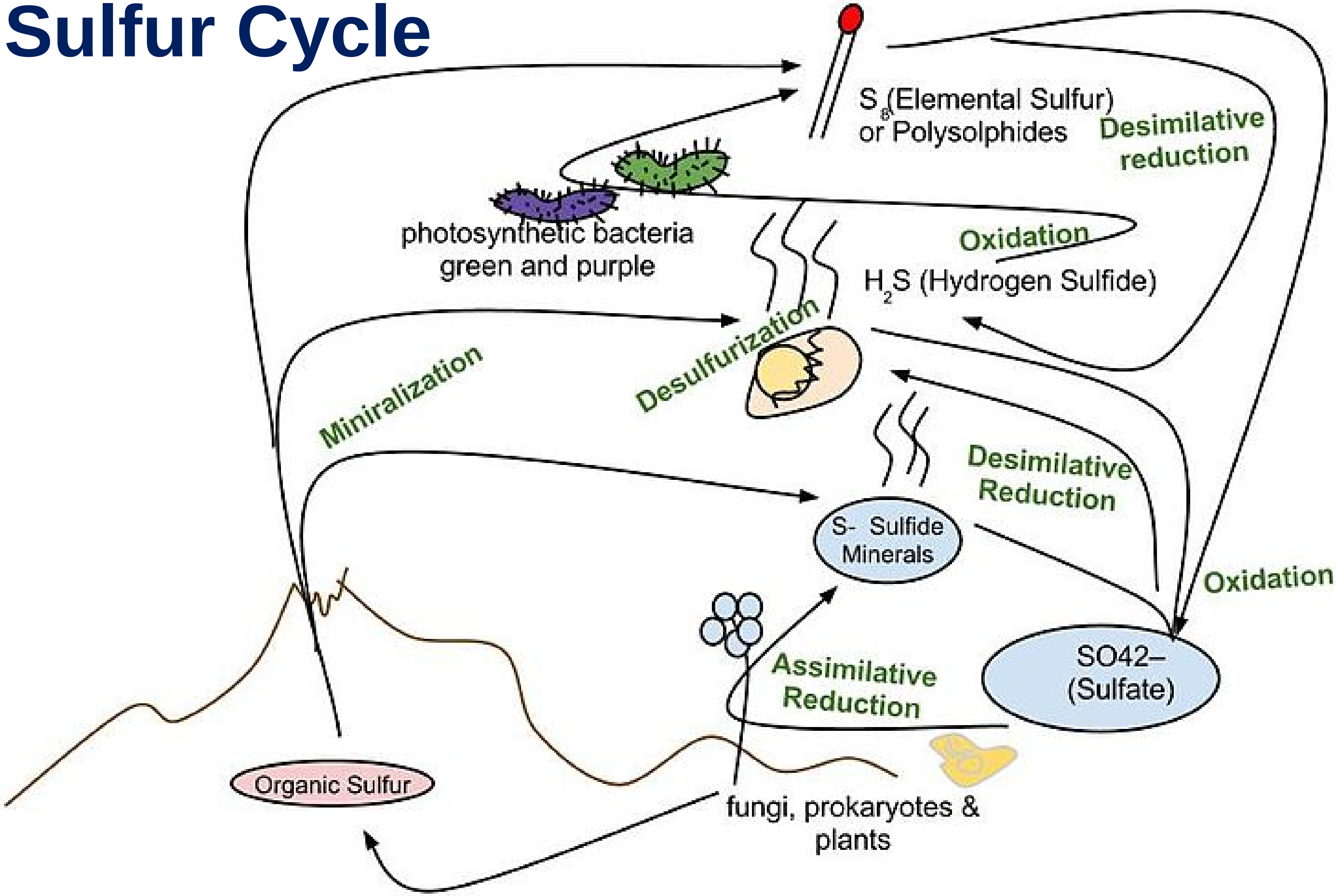
- The collection of processes by which sulfur moves between minerals and living systems.
- Sulfur is found in many minerals.
- Sulfur is also an essential element, being a constituent of many proteins and cofactors.
  - A **cofactor** is a non-protein compound that is bound to a protein and is required for the protein's biological activity. These proteins are commonly enzymes.

Sulfur Cycle Steps

- Conversion of organic sulfur into inorganic forms, such as hydrogen sulfide (H_2S), elemental sulfur, and sulfide minerals.
- Oxidation of hydrogen sulfide, sulfide, and elemental sulfur (S) to sulfate (SO_4^{2-}).
- Reduction of sulfate to sulfide.
- Incorporation sulfide into organic compounds (including metal-containing derivatives).

http://en.wikipedia.org/wiki/Sulfur_cycle

Sulfur Cycle



http://en.wikipedia.org/wiki/Sulfur_cycle

Sulfur Sinks

- Earth's main sulfur sink is the oceans.
- A large amount of sulfur is found in sedimentary rocks, such as iron pyrite, FeS_2.
- The biosphere is not a major sulfur sink.
- Very little sulfur from natural sources is found in the atmosphere, and the sulfur found there does not spend much time there.
  - Dimethylsulfide, $(CH_3)_2S$ or DMS, is produced in dying phytoplankton cells in the shallow levels of the ocean. It is responsible for the distinctive "smell of the sea" along coastlines.
  - DMS is the largest natural source of sulfur gas, but still only has a residence time of about one day in the atmosphere and a majority of it is redeposited in the oceans rather than making it to land.

http://en.wikipedia.org/wiki/Sulfur_cycle

Formation of Sulfur Dioxide in Combustion

- Sulfur dioxide is the product of the burning of sulfur or of burning materials that contain sulfur:

$S_8 + 8\ O_2 \rightarrow 8\ SO_2$

$2\ H_2S + 3\ O_2 \rightarrow 2\ H_2O + 2\ SO_2$

$CH_3SH + 3\ O_2 \rightarrow CO_2 + 2\ H_2O + SO_2$

- The roasting of sulfide ores also releases SO_2:

$4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$

$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$

$HgS + O_2 \rightarrow Hg + SO_2$

$4\ FeS + 7O_2 \rightarrow 2\ Fe_2O_3 + 4\ SO_2$

- Volcanic eruptions, which involve a combination of these reactions, produces the largest amount of sulfur dioxide. They can release millions of metric tons of SO_2.

Sulfur Contribution to Acid Rain

- **Acid rain** is a rain or any other form of precipitation that is unusually acidic, meaning that it possesses elevated levels of hydronium ions, H_3O^+, and therefore have a low pH.
- Acidic water can have harmful effects on plants, aquatic animals, and infrastructure.
- Combustion of compounds containing sulfur yield sulfur dioxide, SO_2. In the gas phase, sulfur dioxide forms sulfuric acid, H_2SO_4.

$$SO_2 + OH\cdot \rightarrow HOSO_2\cdot$$

$$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

Sulfur Contribution to Acid Rain

- Sulfur dioxide dissolves in water to form sulfurous acid, which forms hydronium, hydrogen sulfite, and sulfite ions:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

- Sulfuric acid and sulfurous acid form hydronium ions

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

$$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$$

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$$

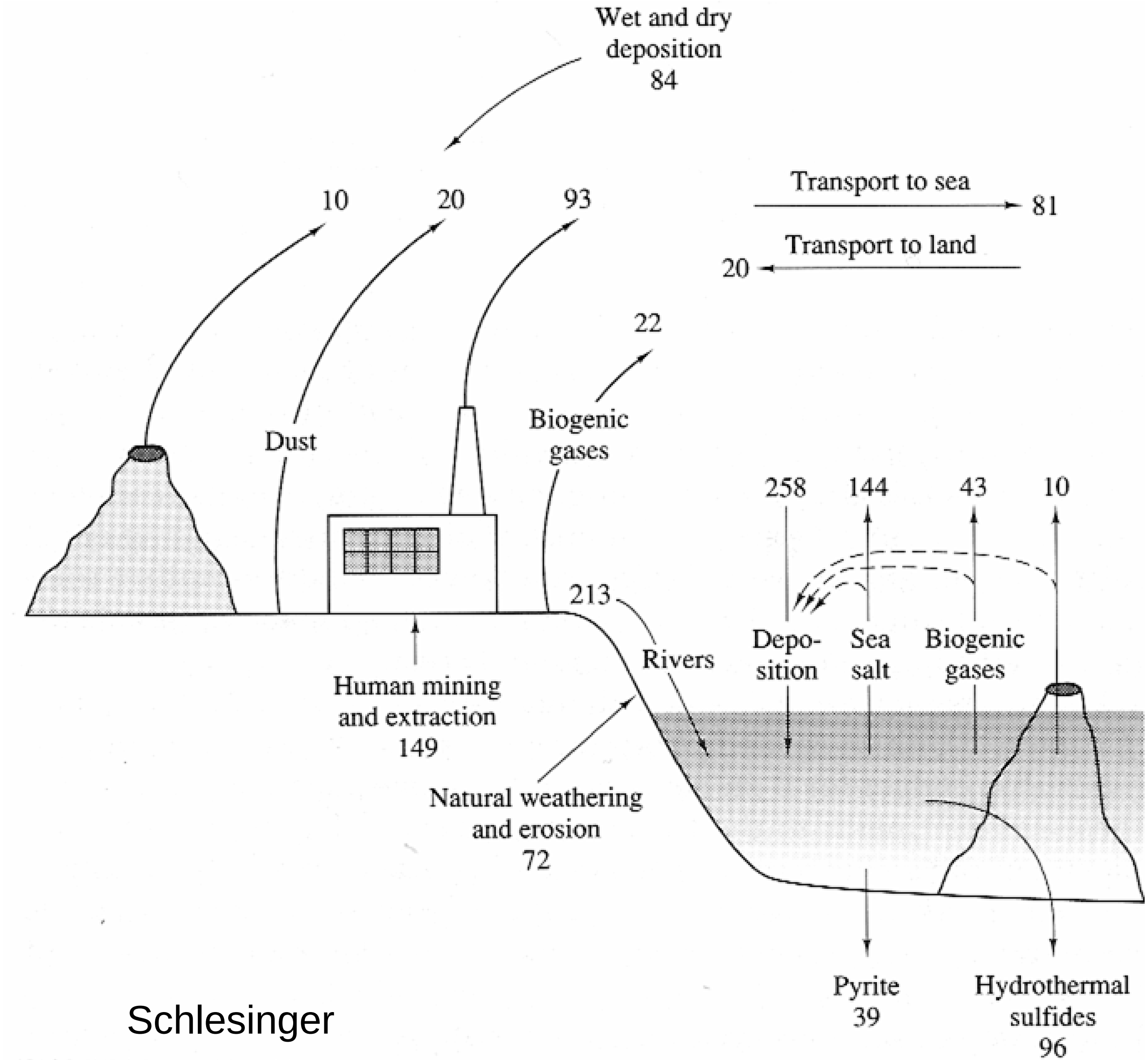
- The pH can drop to 4.3 or lower

Human Impact on Sulfur Cycle

- Burning of coal, natural gas, and other fossil fuels increases the amount of S in the atmosphere and ocean.
- Over the most polluted areas, there has been a 30-fold increase in sulfate deposition.
- We are mining coal and extracting petroleum at a rate that adds 150×10^{12} gS/yr to the sulfur flux, which is more than double the rate of 100 years ago.

http://en.wikipedia.org/wiki/Sulfur_cycle

Global S Cycle
Tg_S, Tg_S/y



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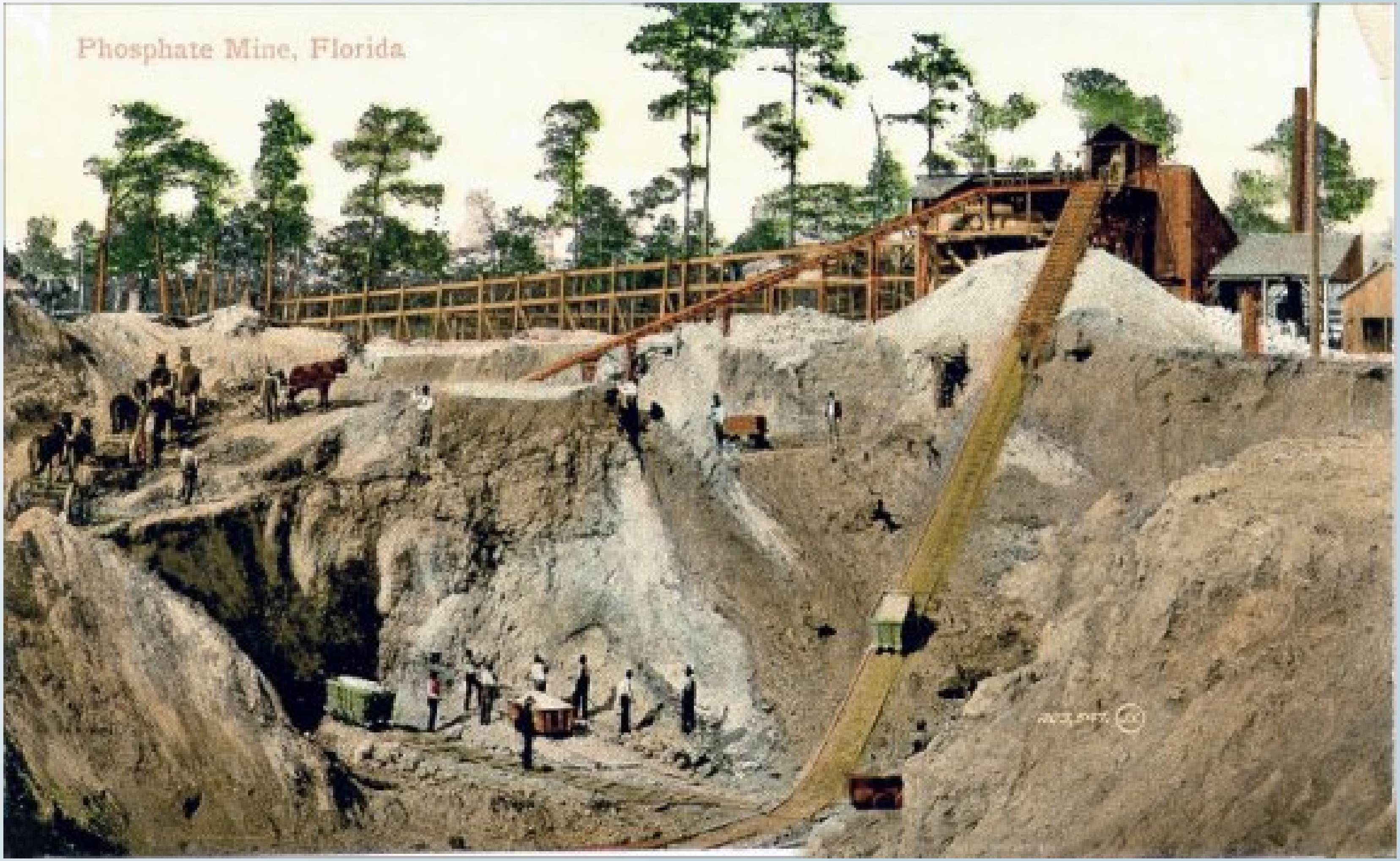
Phosphorus Cycle

- Describes the movement of phosphorus, P, through the lithosphere, hydrosphere, and biosphere.
- The atmosphere does not play a significant role in the movement of phosphorus, because phosphorus and phosphorus-based compounds are usually solids at the typical ranges of temperature and pressure found on Earth.
- Without link to atmosphere, the P cycle is driven only by weathering, uplift, and sedimentation.
- Phosphorous species not very water soluble, so flows in biosphere are relatively small.
- Soil microorganisms act as sinks and sources of available P in the biogeochemical cycle.

Phosphorus

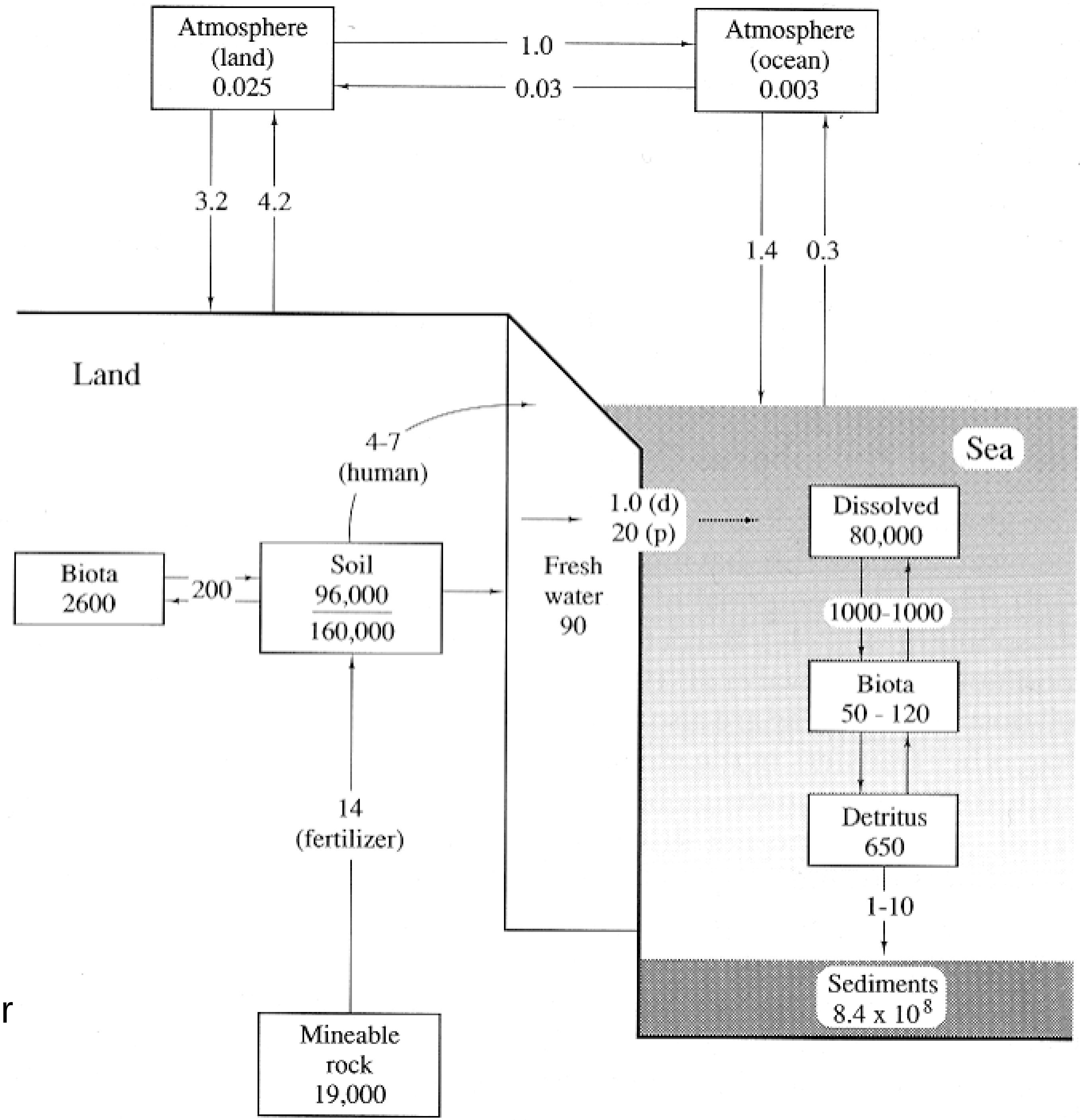
- Important in DNA, RNA, bone formation
- Biomass N:P $\approx$ 10, but P is often the limiting nutrient.
- Recycling of P between living and dead biomass is very strong, especially in the ocean.
- Main human source is mining of phosphate minerals (e.g. $Ca_3(PO_4)_2$).

Phosphate Mining



Global P Cycle

Tg_P, Tg_P/y



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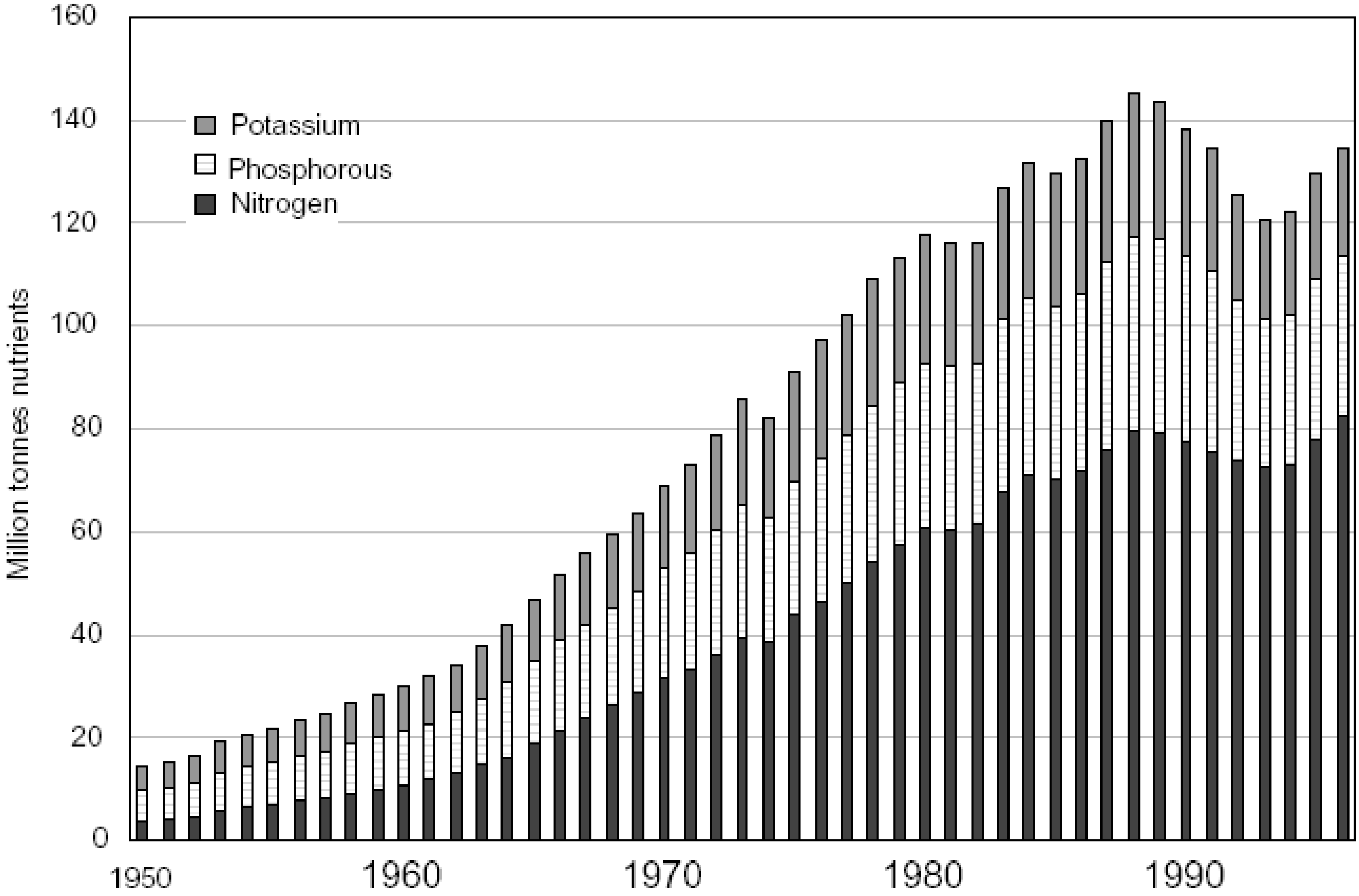
Limiting Nutrient

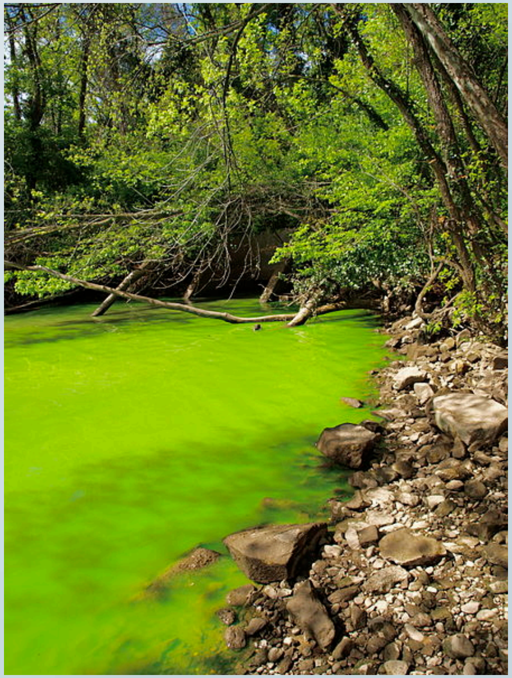
- Limiting nutrient = Nutrient that constrains the productivity of biomass in any particular environment.
  - Desert → H_2O
  - Other terrestrial ecosystems → N, P
  - Freshwater ecosystems → P
  - Oceans → Fe
- Limiting nutrient is often the leverage point where human-induced changes manifest themselves most rapidly

Global Production of N, P, K Fertilizers

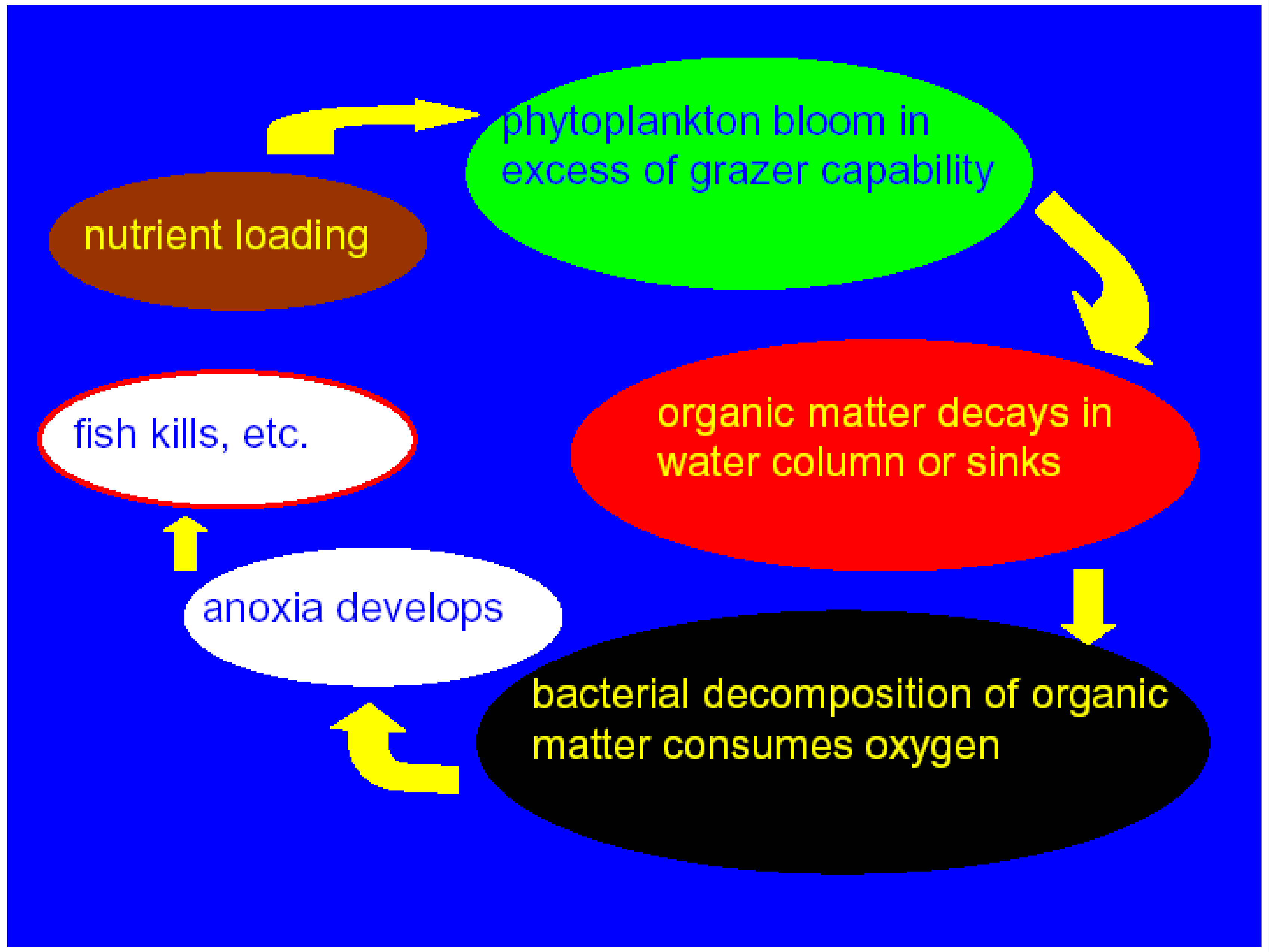


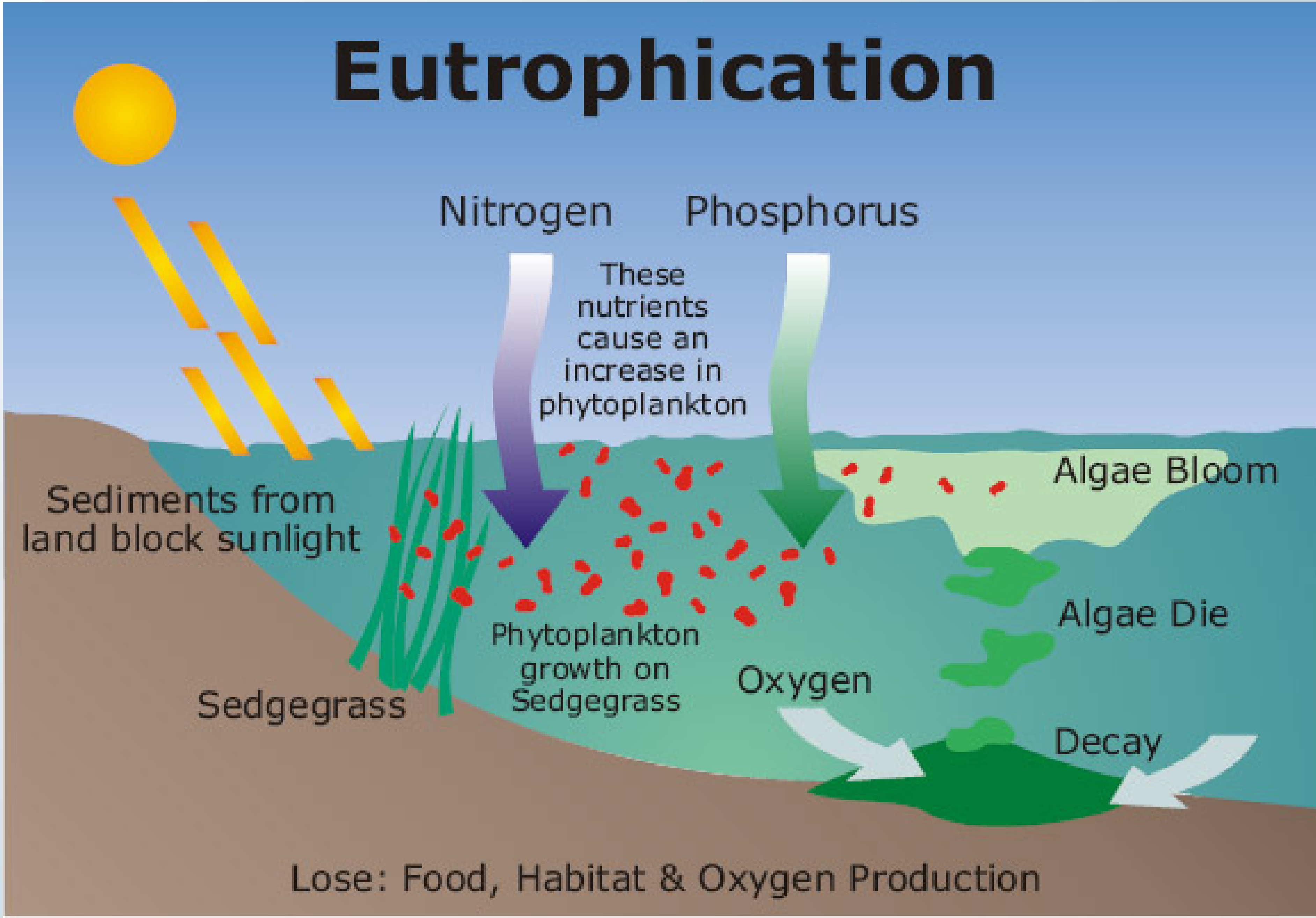
Human Effects on Phosphorus Cycle

- Human interference in the phosphorus cycle occurs by overuse or careless use of phosphorus fertilizers. This results in increased amounts of phosphorus as pollutants in bodies of water resulting in excessive algae growth.
- Surface and subsurface runoff and erosion from high-P soils may be major contributing factors to fresh water eutrophication.



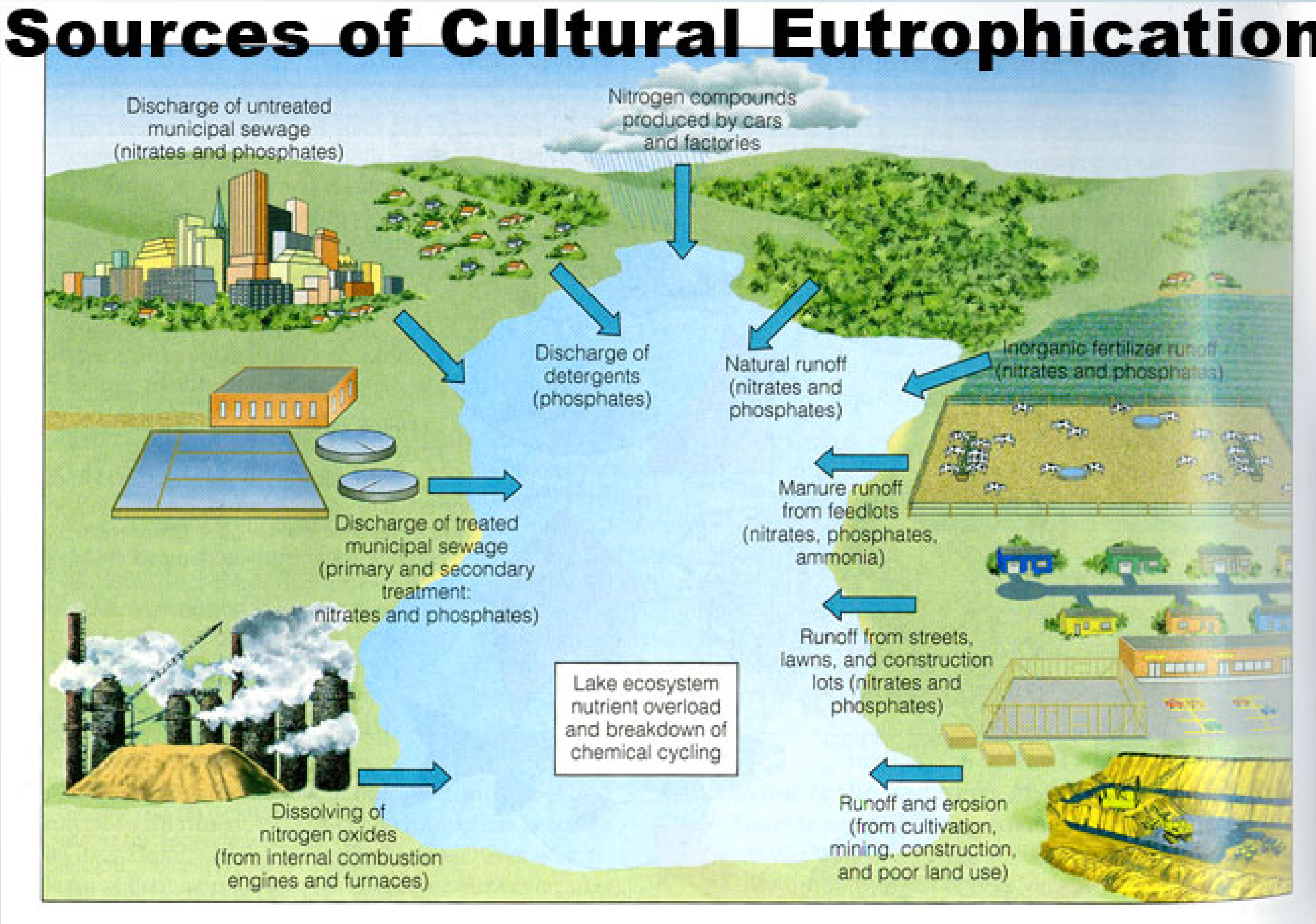
The eutrophication of the Potomac River is evident from the bright green water, caused by a dense bloom of cyanobacteria.


phytoplankton bloom in excess of grazer capability
nutrient loading
organic matter decays in water column or sinks
fish kills, etc.
anoxia develops
bacterial decomposition of organic matter consumes oxygen



Eutrophication
Nitrogen
Phosphorus
These nutrients cause an increase in phytoplankton
Algae Bloom
Sediments from land block sunlight
Algae Die
Phytoplankton growth on Sedgegrass
Oxygen
Sedgegrass
Decay
Lose: Food, Habitat & Oxygen Production

Eutrophication



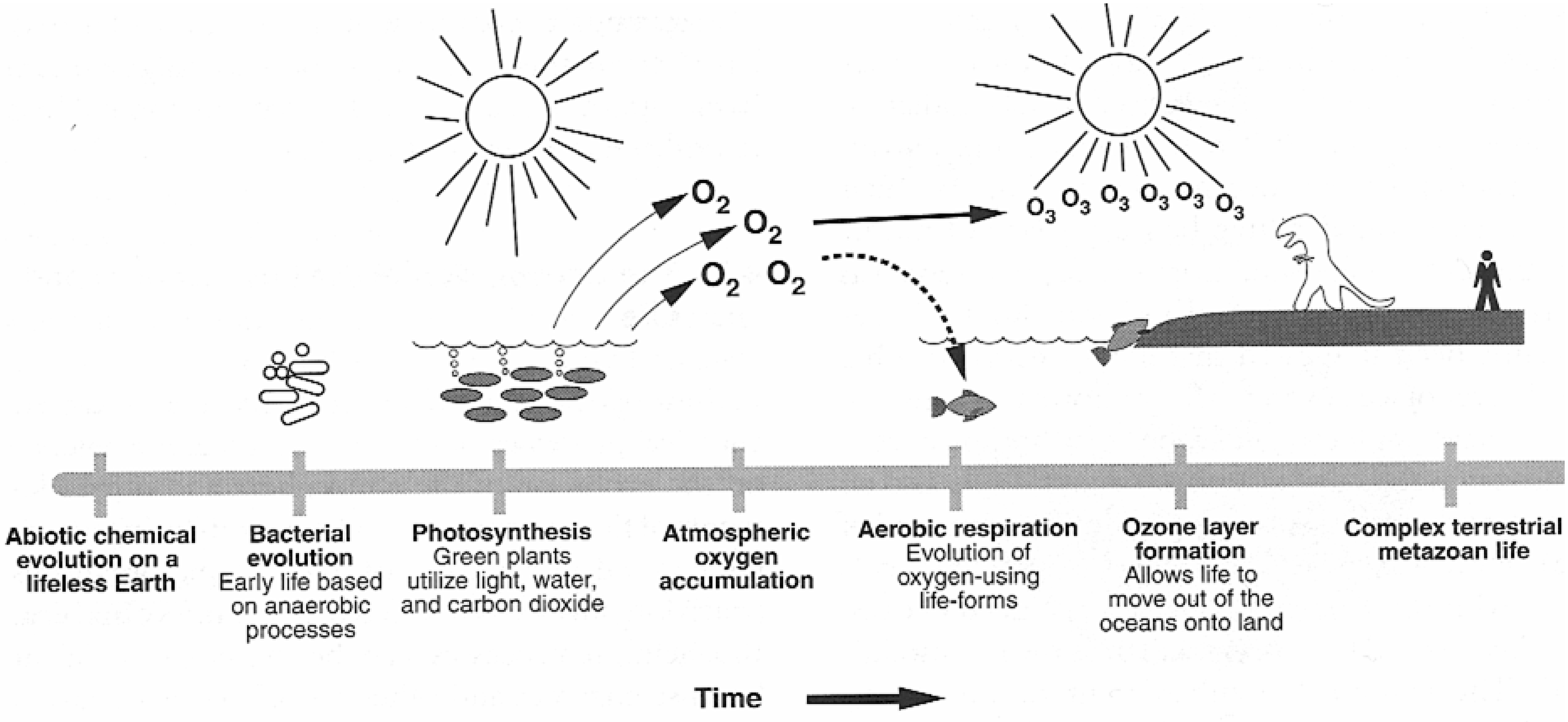
seasonal hypoxia in the Gulf of Mexico is caused by excess nutrient loading in the Mississippi River outflow

"Dead Zones"

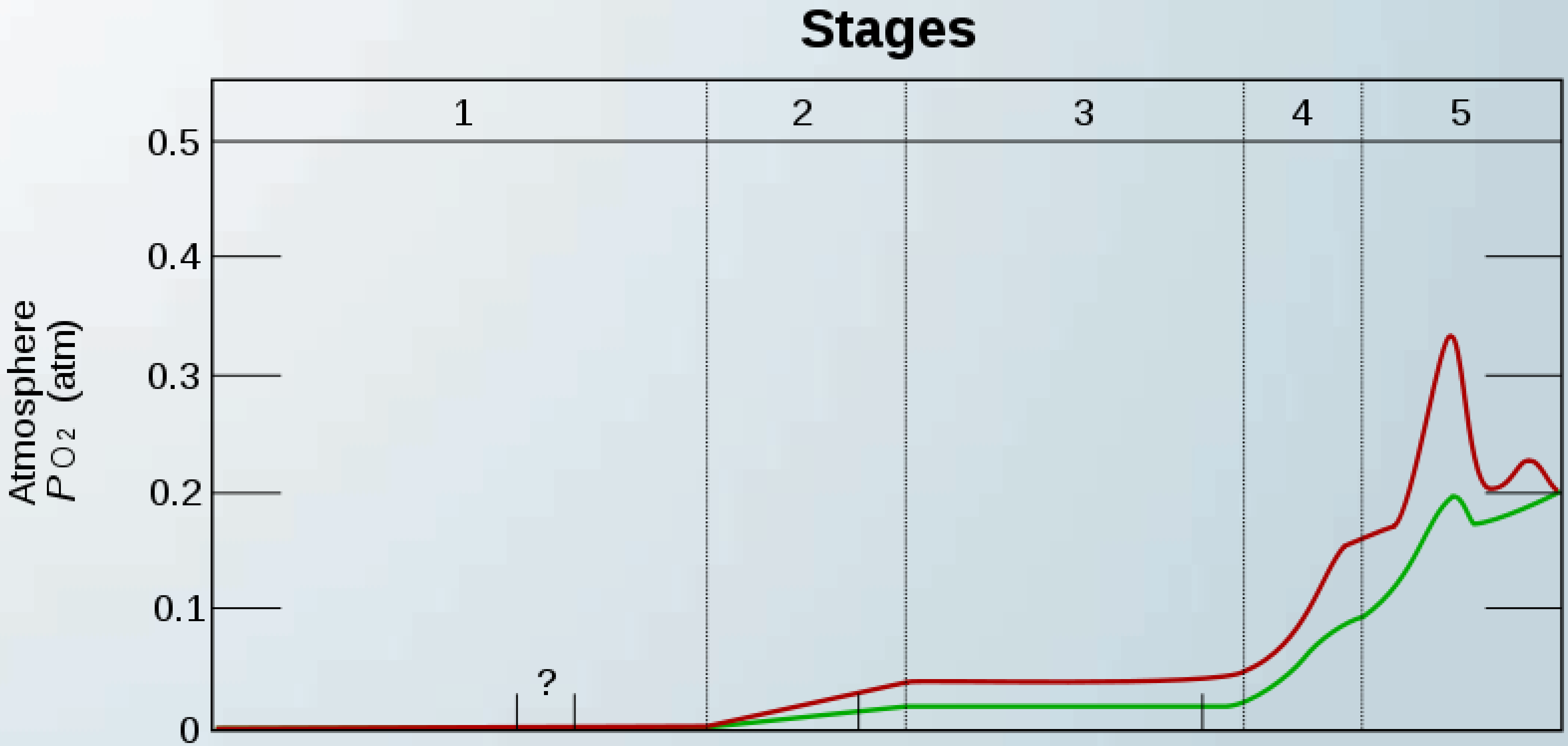
History of Oxygen, O_2

- Free oxygen gas was almost nonexistent in Earth's atmosphere before photosynthetic archaea and bacteria evolved. Free oxygen first appeared in significant quantities between 2.5 and 1.6 Gy ago.
- At first, the oxygen combined with dissolved iron in the oceans to form banded iron formations.
- Free oxygen started to outgas from the oceans 2.7 Gy ago, reaching 10% of its present level around 1.7 Gy ago.
- About 1 Gy ago, O_2 began to accumulate in atmosphere, forming UV-absorbing ozone layer.
- By 500 My ago, O_2 concentration $\approx$20%
- O production balanced by C sequestration

Evolution of Life



History of Oxygen, O_2



O_2 build-up in Earth's atmosphere: 1) no O_2 produced; 2) O_2 produced, but absorbed in oceans & seabed rock; 3) O_2 starts to gas out of the oceans, but is absorbed by land surfaces and formation of ozone layer; 4–5) O_2 sinks filled and the gas accumulates.

http://en.wikipedia.org/wiki/Oxygen

Life and the Physical Environment

- Accumulation of O_2 made respiration possible

  $$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

- $O_2 \leftrightarrow O_3$ makes terrestrial life possible
- Life regulates other gas concentrations that control physical environment:
  - Atmospheric concentrations of CO_2, CH_4, N_2O, which affect climate, are largely determined by the biosphere.
- Gaia hypothesis: that life and the physical environment are tightly interacting, stable system.