Biogeochemical cycles: 1. Introduction

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The interplay between biology and geology

- Compare chemistry of Mars and Venus with that of Earth and the reactions dealing with oxygen-containing molecules
- All 3 planets can be classified as “Type 10” meaning that they are theoretically suitably positioned in the solar system to support life
- The Earth has been labelled with the “Goldilocks syndrome” – the place most comfortable for life out of these 3 planets

What does the fairy story of Goldilocks tell us?

Mars (too cold) Earth (just right) Venus (too hot)

Not too hot, not too cold, but ”Just right!” as Goldilocks said about the Little Bear’s porridge (and that was all eaten up – oops!)

Which all goes to show that, actually,
women are from Mars and men are from Venus
– as if we didn’t know!

What makes the Planet Earth Special?

The Earth has a number of features which mark it out as a special planet.

These include:

- The composition of the atmosphere
- The presence of water in all its states
- The presence of a natural carbon sink as a result of the interplay of biology and chemistry in producing biogenic rocks (The White Cliffs of Dover, for example)
- The robustness of life in overcoming catastrophes
- The presence of seismic activity and plate tectonics – demands an active core which should probably be magnetic and polarised
- The capture of phosphorus to enable ATP formation – the battery of life

All of this is relatively easy when we stay at the single-celled organism level…

The human dimension involves needing to know, measuring and quantifying – this is what scientific endeavour is all about.

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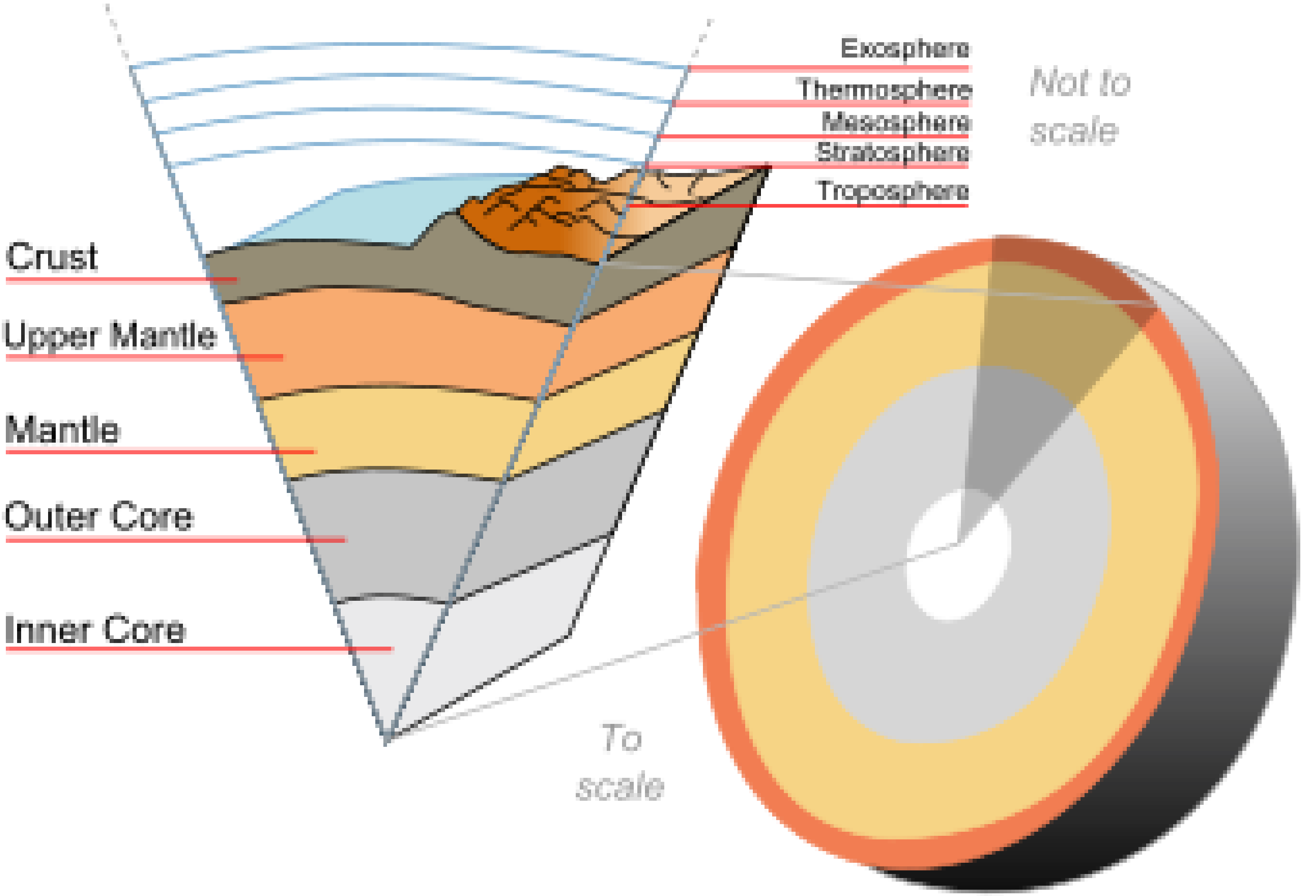
Earth may well be the most chemically interesting planet we can ever visit

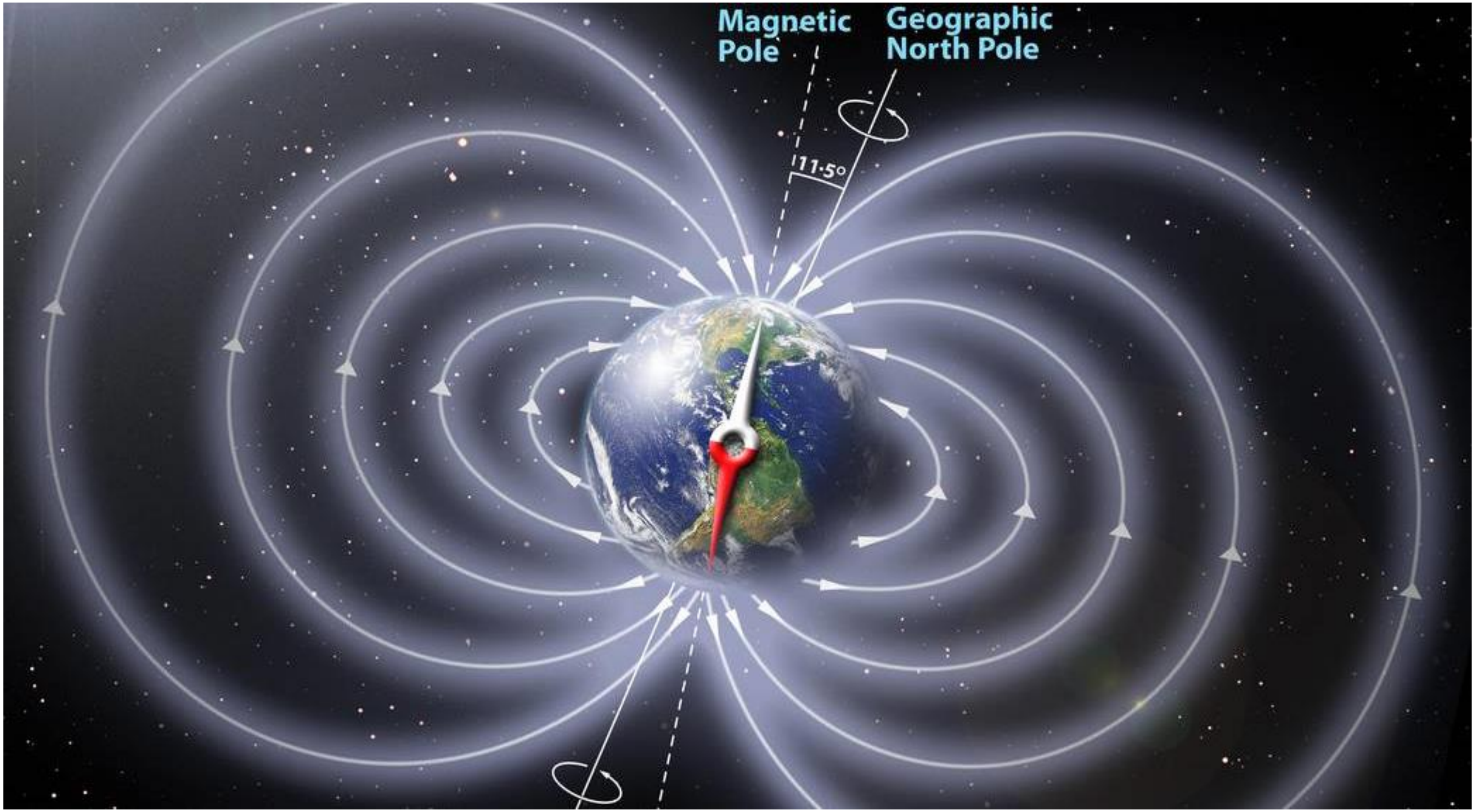
- Abundance of chemical elements across the universe compared with Earth. Evidence for complex molecules elsewhere
- Because of the size of the Universe it is difficult to judge its current composition – we are always looking back into history!
- Composition of the Solar System is easier
- We know that Earth has 92 naturally occurring elements and that we can produce artificial ones as well as unstable isotopes

The core composition of the Earth might be a deciding feature for stabilising the environment

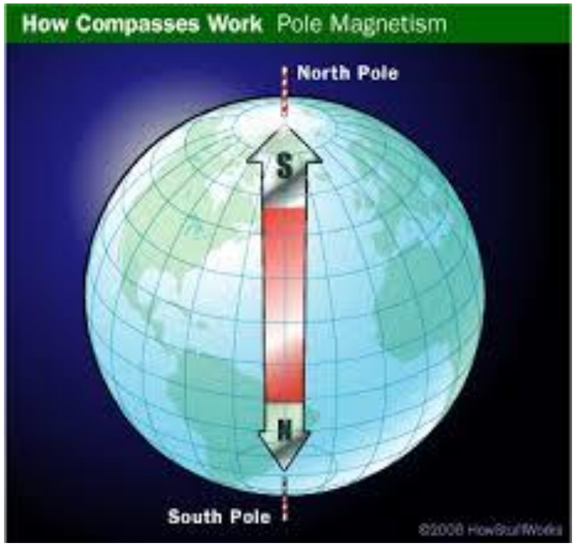


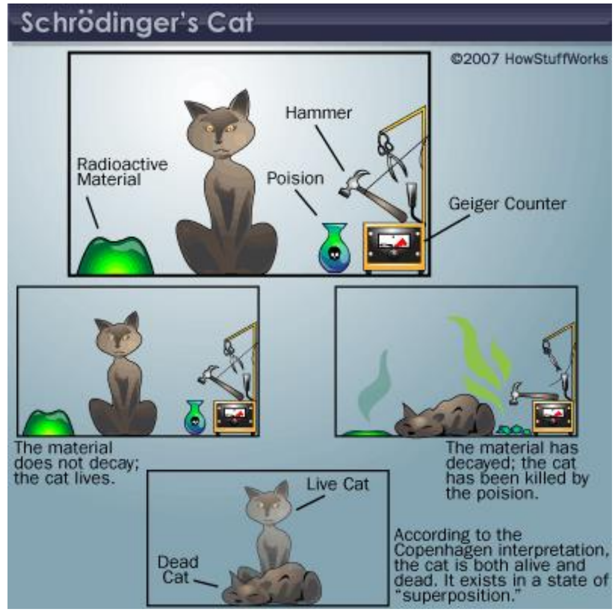
The magnetic core is important for protecting the surface from harmful solar wind - gamma and higher radiation – whilst the protective ozone layer blocks out the lower energy, but harmful to life, uv radiation

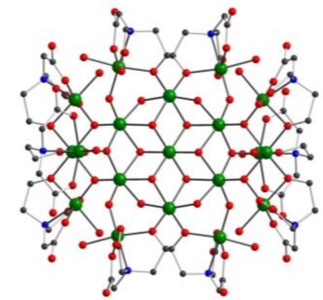
A representation of the Earth's Magnetic Field



Magnetism at many levels



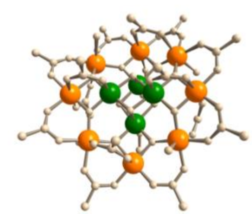


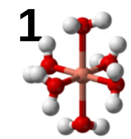


Macroscopic ⟷ Nanoscopic

Permanent magnets	Micron particles	Nanoparticles	Clusters	Molecular clusters	Individual spins

$S = 10^{20}$ 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1





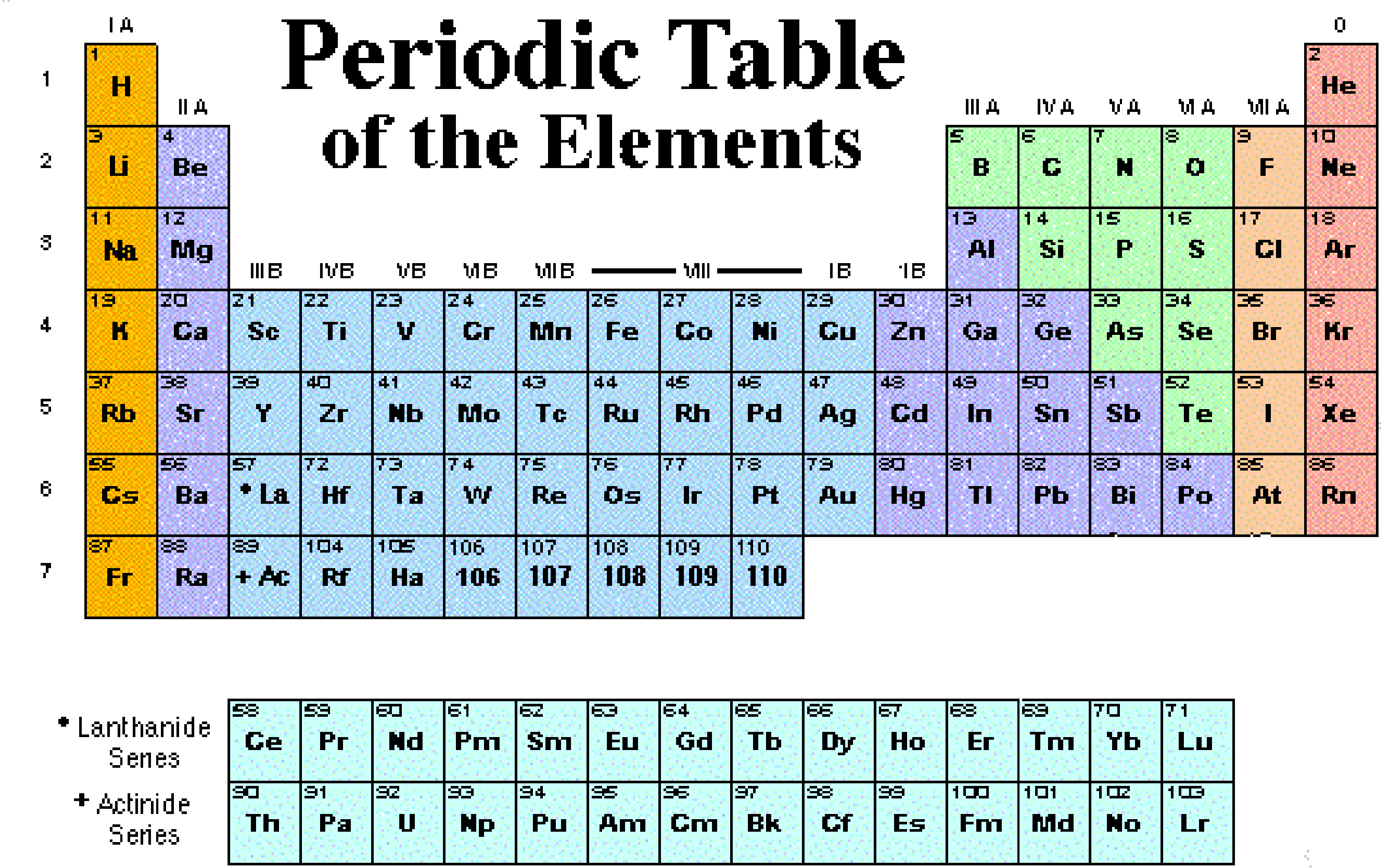
What does the magnetic core do?

- The magnetic field around the Earth protects us from the harmful gamma rays of the "Solar Wind" by deflecting them away from the surface.
- This effect is seen most markedly at the poles and gives rise to the Northern (Aurora Borealis) and Southern (Aurora Australis) lights.
- Furthermore, the magnetic field prevents the solar wind from "blowing away" the atmosphere.
- The lack of an active (dynamic) magnetic core on Mars explains its very thin atmosphere.

Aurora Borealis

Aurora Australis

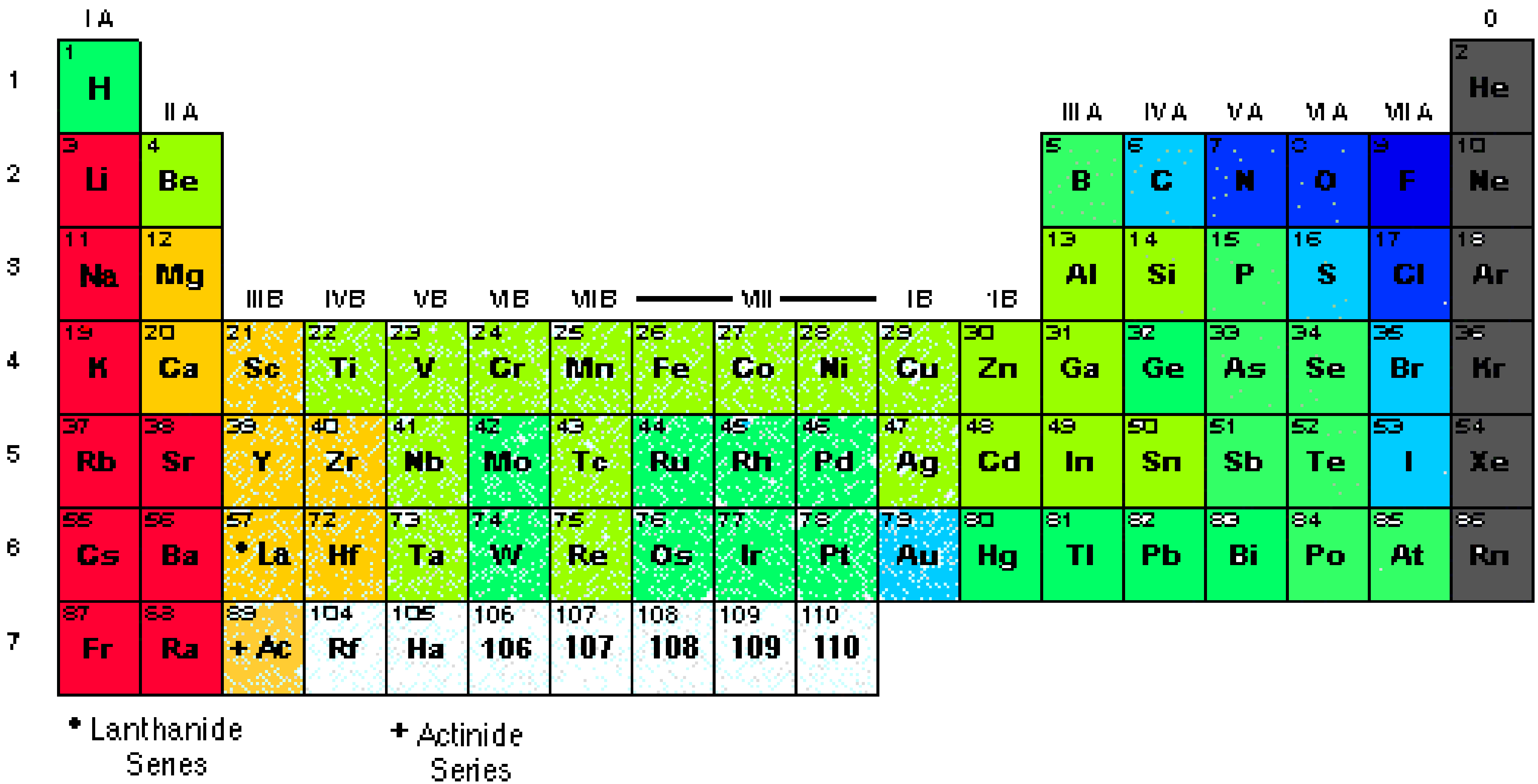
Periodic table according to element type



Abundance of chemical elements available on Earth

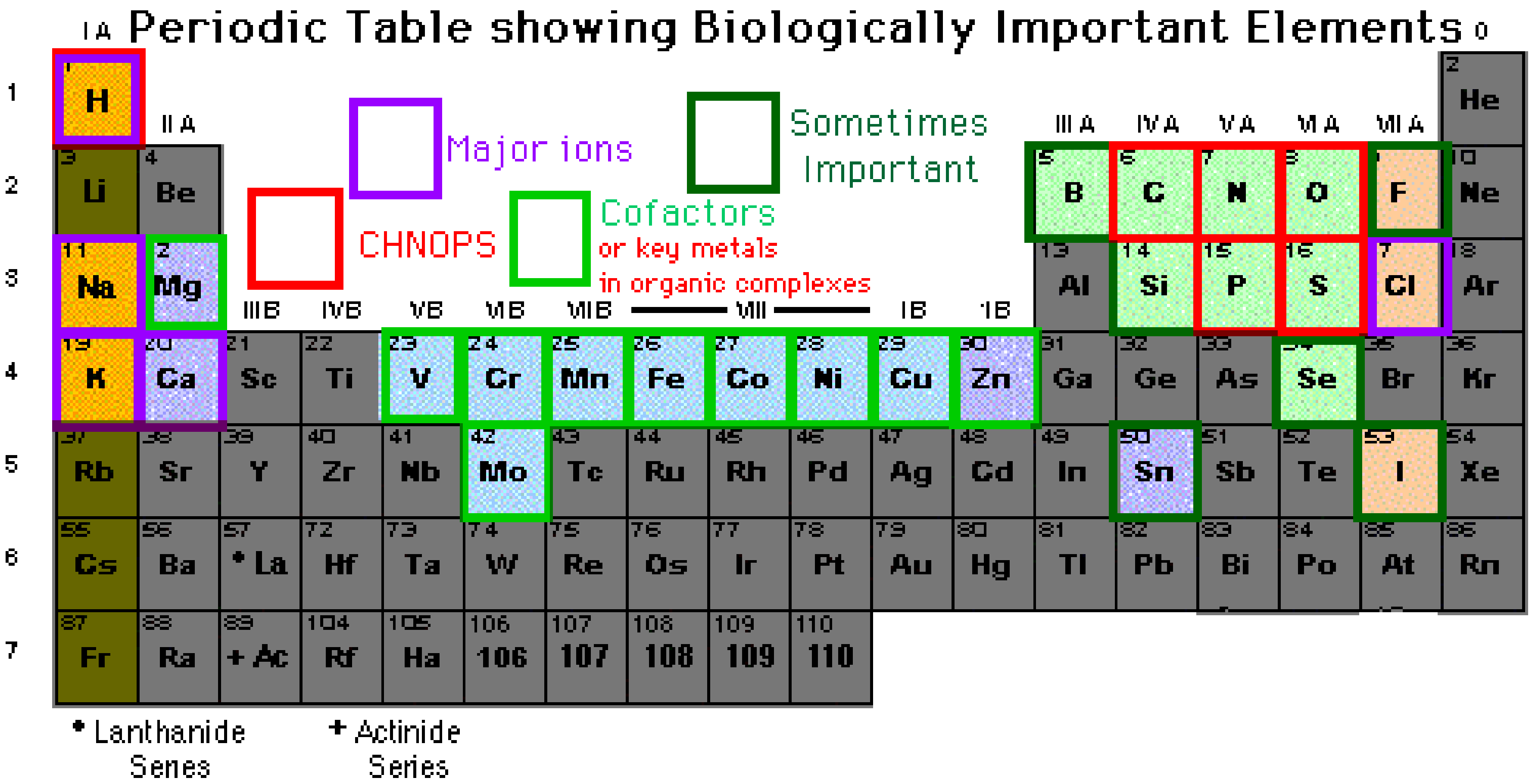
- Periodic table so far highlighting the main elements, their electronegativities and those important in biology
- We can suppose that these elements also exist on the other planets since all apart from H, He (and Li) were formed through combinations of these via nuclear fusion as the solar system formed
- From our current perspective, the Universe is composed of 74 % H and 24 % He – but remember we are looking back in time
- This means that what we see in terms of elements on Earth is somehow special since our most abundant elements are Si, O Al and Fe (we need to remember the difference between the atmosphere, biosphere and geosphere)

Periodic Table Showing Electronegativities



Dark blue: highest electronegativity, red, lowest. Noble gases set at zero

Biologically Important Elements



26 elements are important to living things: the big six, C, H, N, O, P, S (CHNOPS) account for 99% of atoms by number (H most abundant) in the human body. In the remaining 1 % of so-called trace elements only 0.01 % come from the d-block.

Interaction of biological systems with available elements leads to the creation of incredibly complex molecular systems

- Proteins, DNA, ATP, Carbohydrates, Polymers etc
- The use of carbon to build complex architectures is a special feature of chemistry on Earth. Although large C-C bonded structures can be found in interstellar media, molecules combining C, H, N, O plus others (P for ATP and DNA etc) may be a special marker for the presence of life.
- Initially these may have been formed by template reactions involving mineral fragments

Geology: Cleveland Volcano Alaska photographed from the ISS, May 2006

Biogeochemical cycles – Geological, Chemical and Biological Evolution on Earth

- **Chemical Evolution** – In comparison with Earth's neighbouring planets of Venus and Mars, chemistry even without the presence of life was more complex than appears to be the case on either of these two planets.
- Several factors may have contributed to this.
- **Geologically**, heavy seismic activity brought core elements to the surface of the Earth as part of molten rock (magma) and gases (usually very rich in sulphur).
- Very early **life-forms** evolved which feed on purely "inorganic" substances and give rise to the idea of ABIOGENESIS (or **biopoiesis)** which probably occurred between 3.9 and 3.5 billion years ago, in the Eoarchean era, which succeeded the Hadean era when the Earth was essentially molten.

Geology, biology and chemistry meet: Stromatolites – the world's first trolls?

These look like rocks : they are "living rocks" combined in symbiosis with photosynthesising cyanobacteria and have been extant for over 3.5 billion years

Biogeochemical cycles – Geological, Chemical and Biological Evolution on Earth

- Maybe the important point is that Geology, Biology and Chemistry can all produce metastable, long-lived (maybe trapped) systems on Earth.
- It is easy to forget that most life relies on symbiosis – if you don’t have the right bacteria in your gut, for example to help you digest cheese, you get nightmares!
- By the way, it is believed that the human ability to continue digesting milk proteins long after infanthood is one of the reasons for our “braininess” and out ability to preserve milk by making cheese has helped us along the way…
- And what happens to this symbiosis when you keel over and die and stop eating cheese?!
- Note that this also applies to the favourite in biology and medicine - and infamously, to domesticated cat-and-mouse-ology – the poor old mouse model…

Biogeochemical cycles
2. Mixing geology and biology leads to great chemistry

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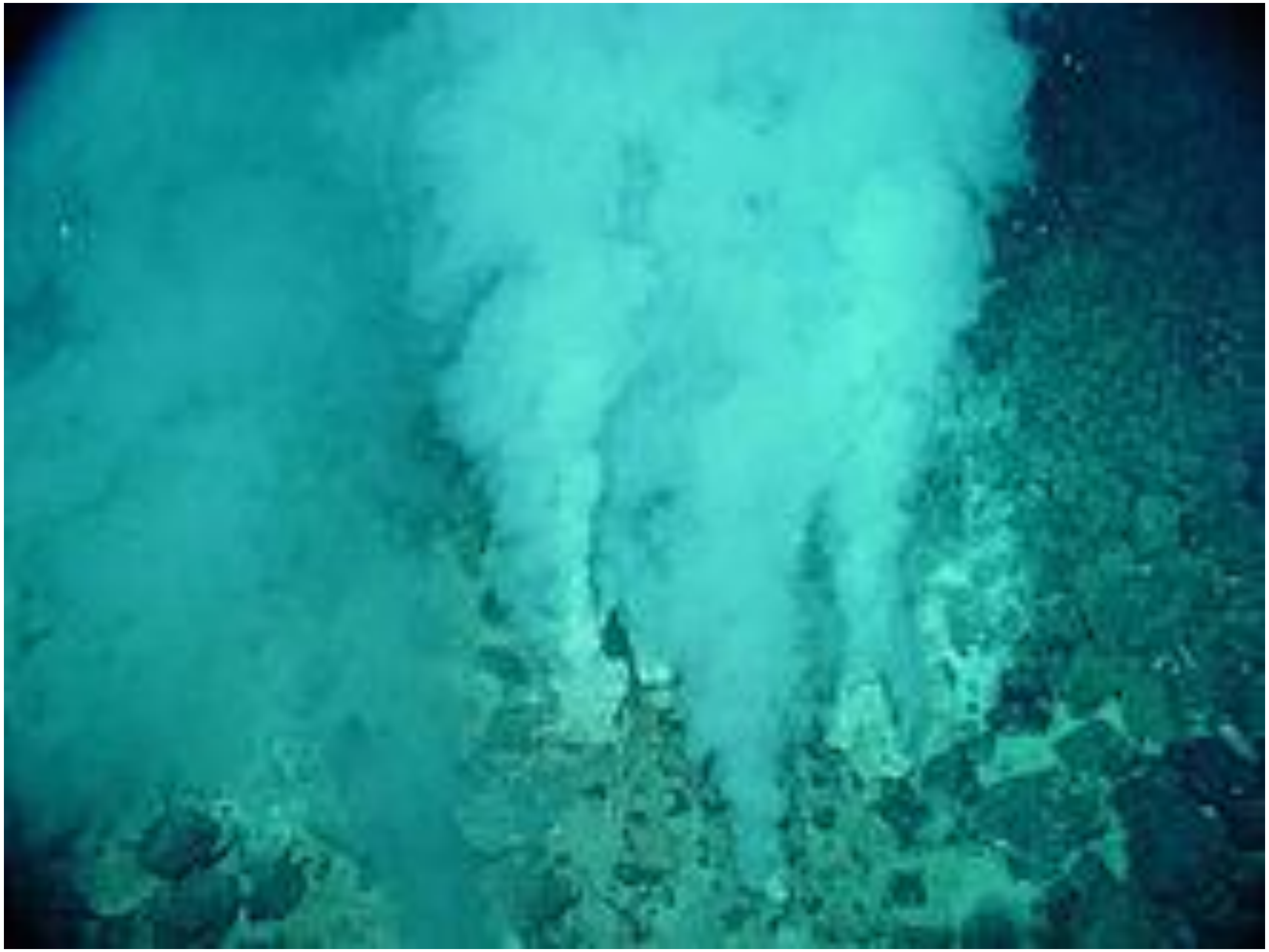
Biogeochemical cycles – Geological, Chemical and Biological Evolution on Earth

- **Chemical Evolution**
- Species such as particulates of FeS_2 (iron pyrites) might act as templates for organic transformations leading to the first molecules for biology.
- Once biology comes into play, the chemistry becomes ever more intricate and task-specific.
- Making and breaking of molecular bonds requires a balancing act in terms of thermodynamic stability, kinetics (speed of the reaction) and availability of the starting materials.

Biogeochemical cycles – Geological, Chemical and Biological Evolution on Earth

- **Biological Evolution** – all the conditions on Earth today seem ideally suited for sustaining life, but we have to bear in mind that what we see is the result of successful adaptations by living organisms to their environment.
- The fact that environmental factors have nearly destroyed life on several occasions in the Earth's history reminds us that the life we see around us represents a compromise adapted to its environment along the lines of "Survival of the fittest" - not Darwin's phrase but quoted by him and first used by Herbert Spencer.
- This refers the system best fitted to adapt to its surroundings and used by Darwin when referring to the specialised adaptations of the bills of finches in the Galapagos enabling them to eat only certain specific foods. The message here is not so much that the finches have remarkable adaptive skills, but rather that they are doomed if their specialised food source disappears as then their adaptation will have led them to a dead-end.

Geological Influences

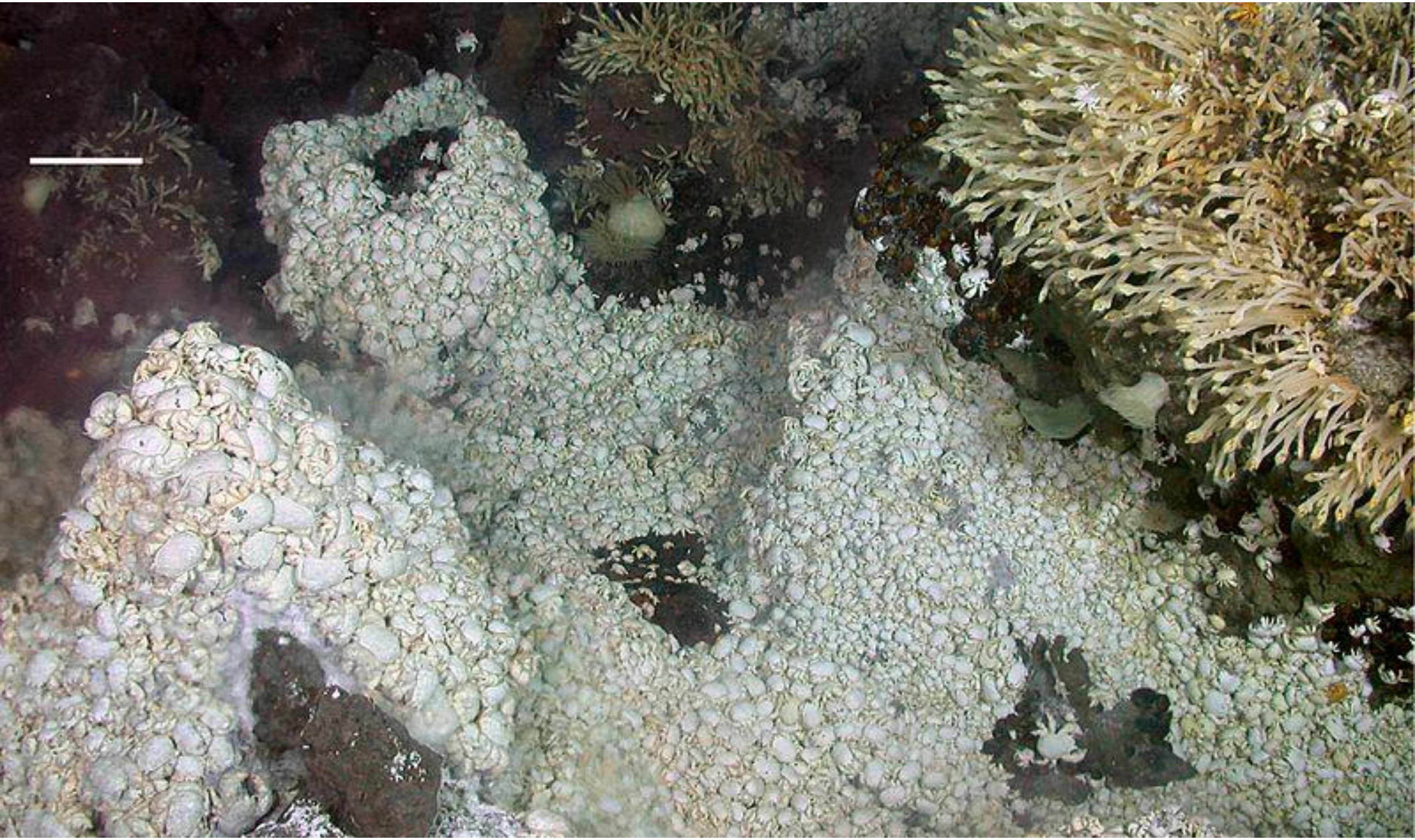


The so-called “Champagne Vent” Northwest Eifuku volcano, Marianas Trench Marine National Monument white smoker

Biogeochemical cycles – the Interplay of Geology, Chemistry and Biology

- Growing evidence that what we like to separate out as Geology, Chemistry and Biology actually act in concert to favour or disfavour conditions for life – this more easily imagined as the result of tipping a delicately poised set of dynamic equilibria.
- Evidence is given by periodic catastrophic environmental events often leading to mass extinctions (the demise of the dinosaurs is an obvious example).
- Need to correlate geological events (tectonic plate movements) with biological (evolutionary) changes and recognise that often the catastrophe is the result of a prevailing unfavourable local chemistry.
- Some life-forms, however, seem to be virtually indestructible!
- So-called extremophile bacteria can withstand very high or very low pressures, survive on nothing more than rocks and if life had ever formed on Mars or Venus may well be still present there.

Unexpected multicelled life near hydrothermal vents



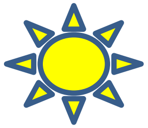
Dense mass of anomuran crab Kiwa around deep-sea hydrothermal vent

Potentially catastrophic biologically-oriented events

- In general, biology affects its environment.
- Compare blood serum with seawater and simple things like chemical redistribution of P
- Chemical entropy – redistribution of elements
- N_2 fixation
- Photosynthesis
- CO_2 balance

Development of photosynthesis released vast quantities of oxygen into atmosphere

Overall reaction looks simple:



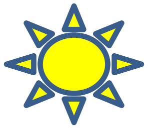
$$nCO_2 + nH_2O \longrightarrow \{CH_2O\}_n + nO_2$$

Simple combination of carbon dioxide and water gives carbohydrates plus oxygen. The dioxygen formed is a byproduct toxic to most forms of the extant bacteria (single-celled organisms) present when photosynthesis was first developed.

However, life evolved to meet the challenge of the presence of the toxic gas and now much of it depends on the presence of oxygen. In particular, the harmful uv-radiation was blocked from the atmosphere by reactions creating an ozone layer and the evolution of multicelled and land-based organisms was favoured.

One thing leads to another – aerobic respiration and CO_2 production

Photosynthesis:



$$nCO_2 + nH_2O \longrightarrow \{CH_2O\}_n + nO_2$$

Respiration and burning fossil fuels:

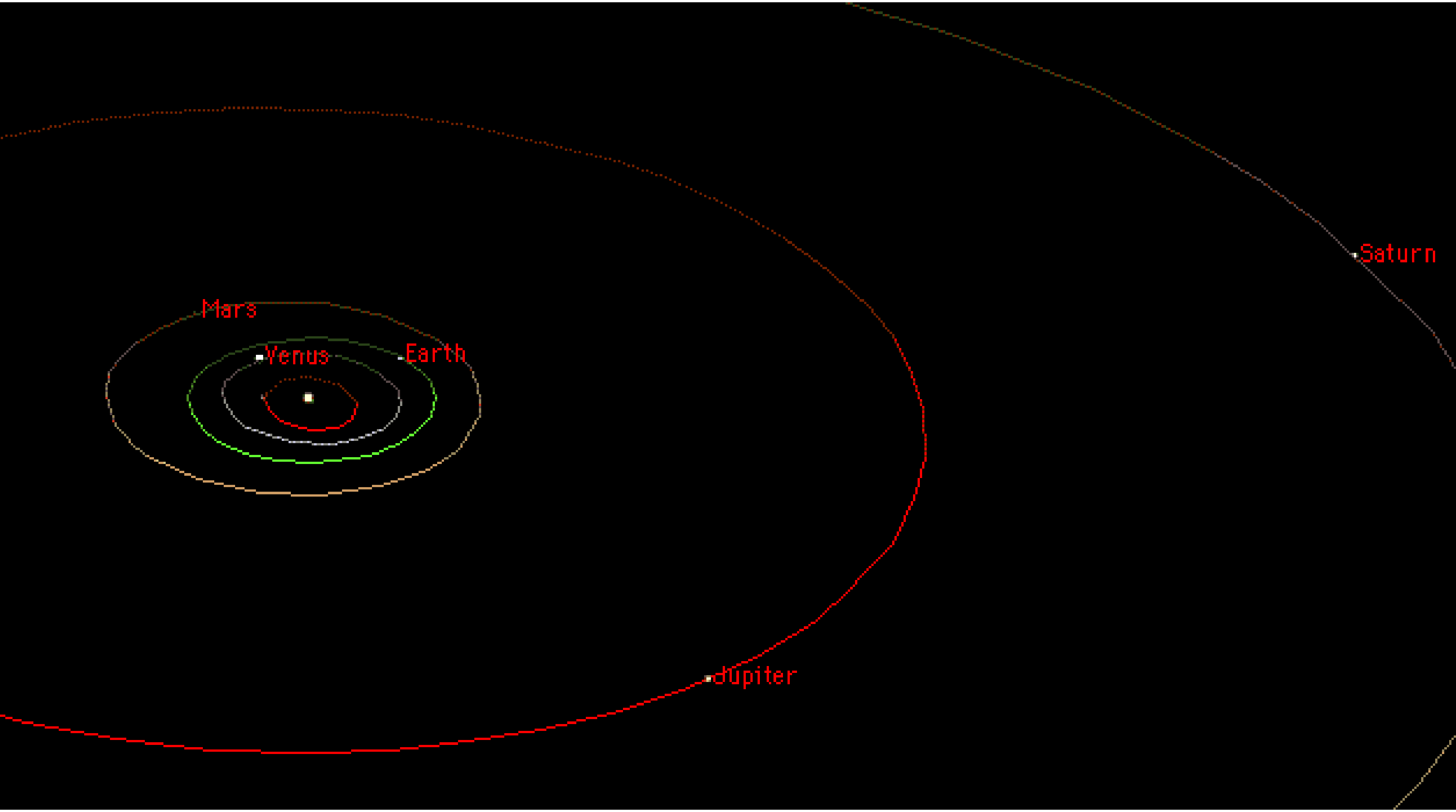
$$\{CH_2O\}_n + nO_2 \longrightarrow nCO_2 + nH_2O + ENERGY$$

Carbohydrates often reduced to hydrocarbons or carbon when in fossil fuels (but not in wood, for example). For organisms the original source is always floral or bacterial derived carbohydrate.

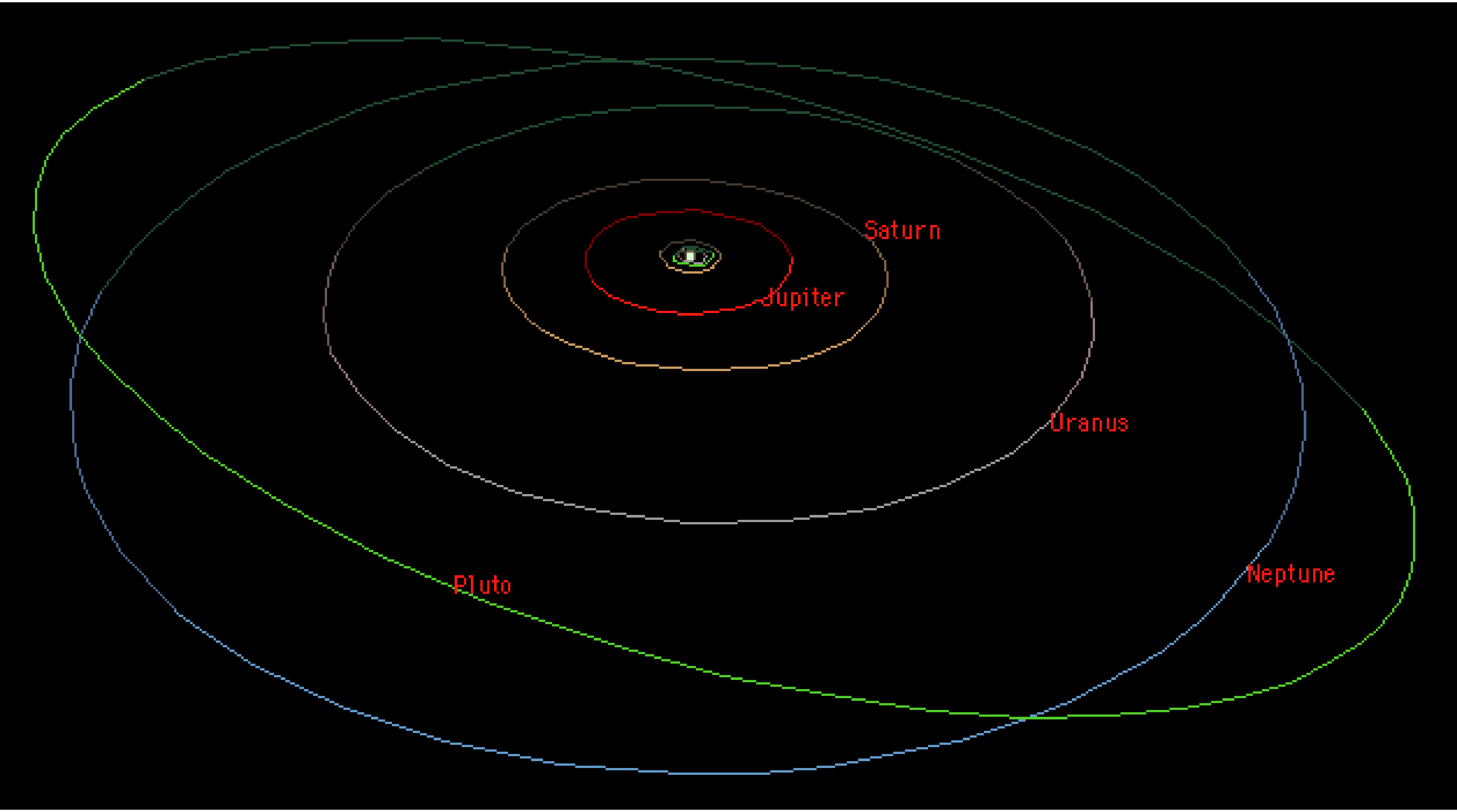
More recently excess greenhouse gases in atmosphere arising from human activities

- Although the greenhouse effect is an important way of keeping the surface temperature of a planet at comfortable levels, only tiny amounts of such gases are required – too much and things can go awry
- The vast majority of the atmosphere of the Earth is made up of nitrogen and oxygen with about 1 % argon and small amounts of other gases
- Contrast Venus and Mars

The Inner Solar System highlighting the Terrestrial Planets

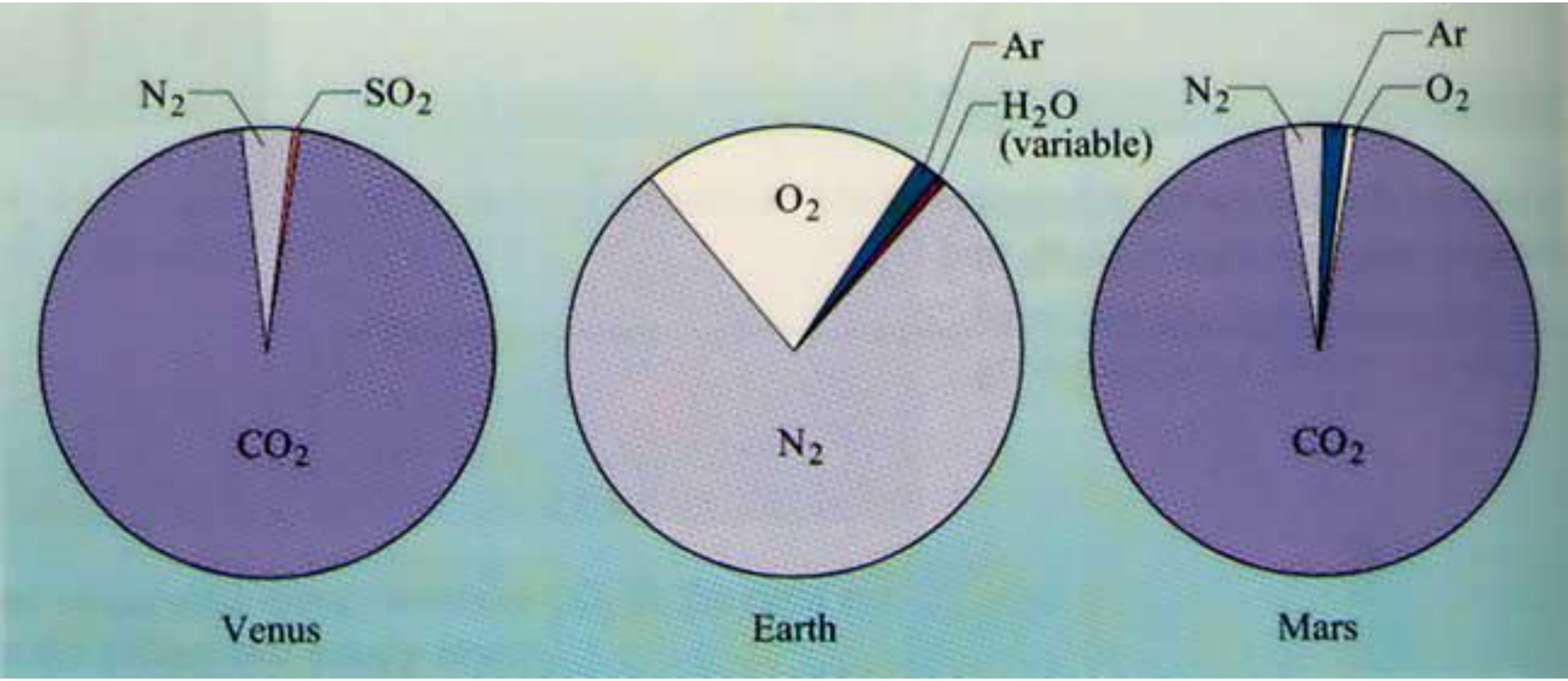


Whole Solar System in Terms of the formerly accepted Nine Planets (i.e. with Pluto)



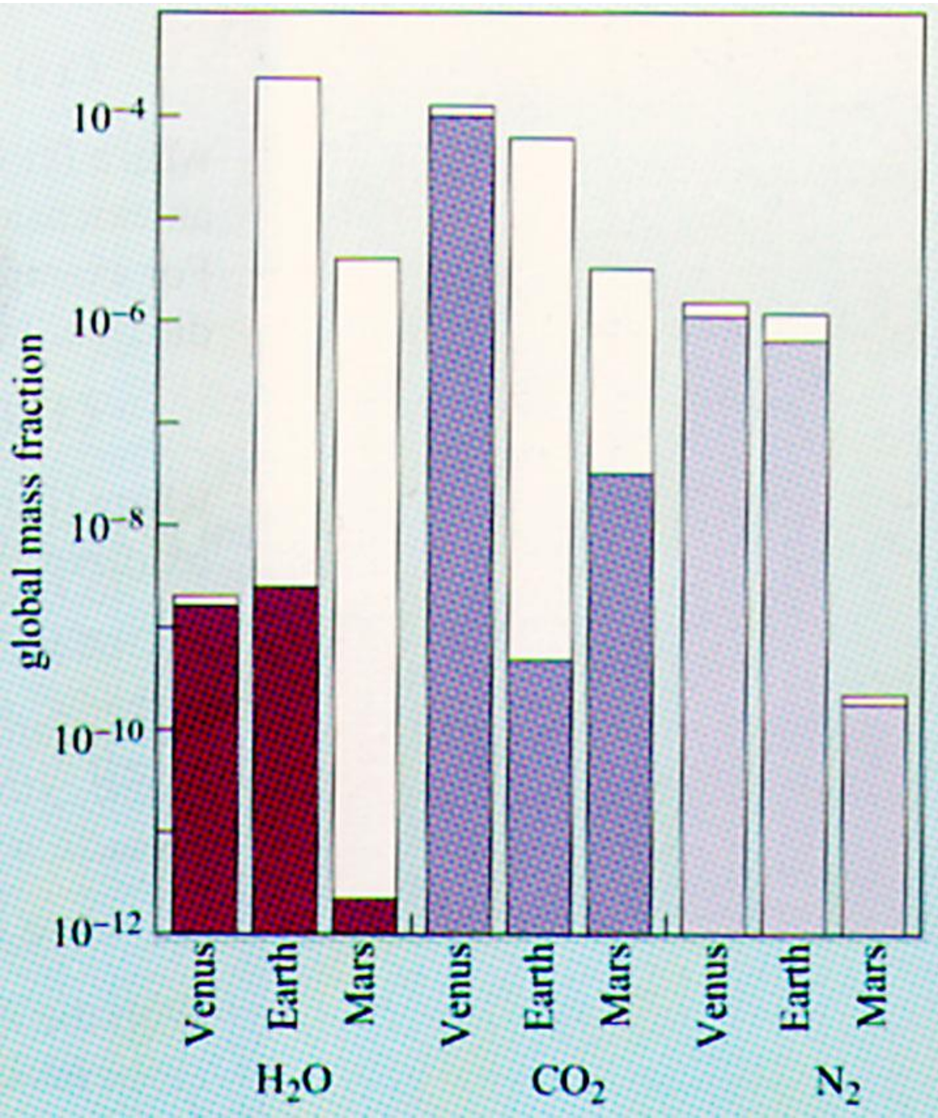
The Planets of the Solar System

Compositions of the atmospheres of the terrestrial planets



The atmospheres of Venus and Mars have huge amounts of carbon dioxide and hardly any nitrogen – the opposite is true for the Earth

Current relative amounts of "Volatile gases" on Venus, Earth and Mars



These bar graphs show the amounts of total volatiles contained within the planets (to the top of the unshaded region) and those in the atmospheres of Venus Earth and Mars (shaded regions).

Three climatic scenarios can be recognised as resulting form the way in which the greenhouse effect has operated:

1. VENUS: Runaway Global Warming
2. EARTH: Ideal
3. MARS: Runaway Refrigeration

The detailed reasoning behind this will be discussed later

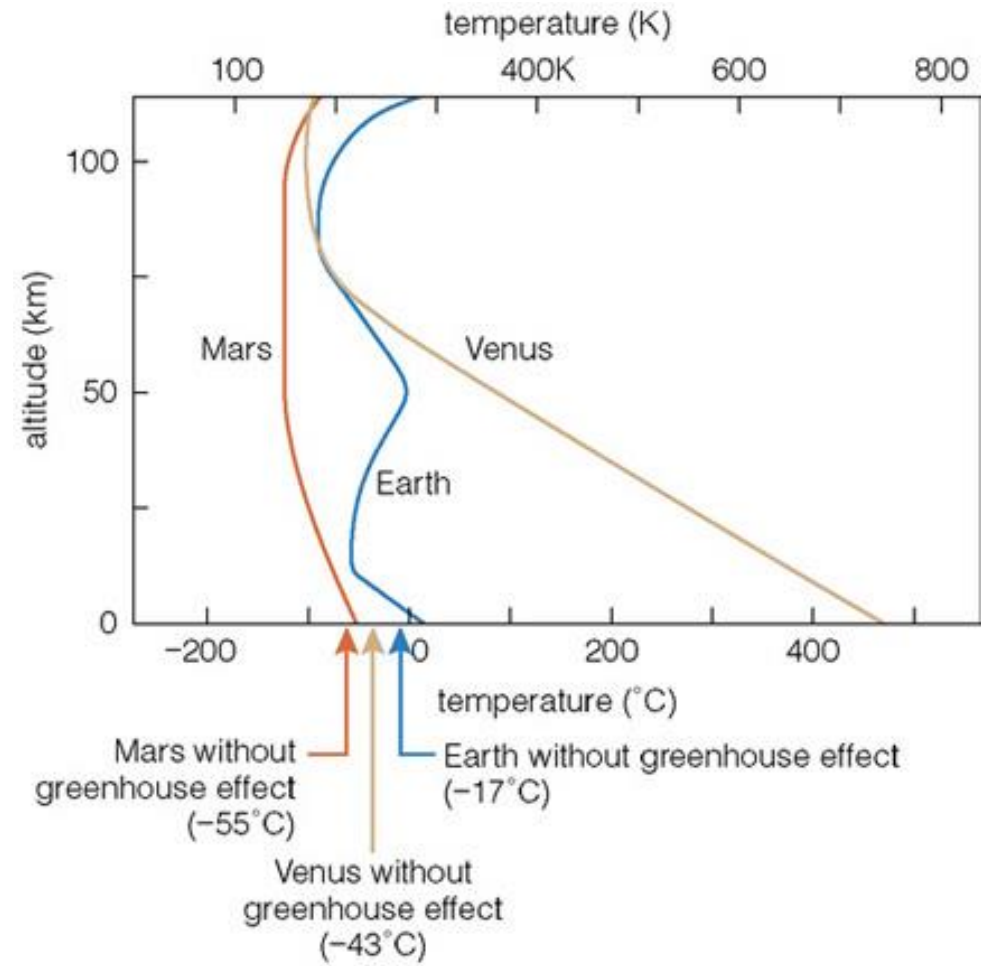
Outlook for terrestrial planets without influence of greenhouse effect

Without any greenhouse effect the terrestrial planets would be inhospitably cold at the surface.

The fact is, just the “right amount” of greenhouse effect is needed to make for ideal living conditions.

Indeed, periodically the Earth goes through a cooling phase (Ice Age) which is challenging for life. Overheating would be even more challenging!

The question is whether biological (human) activity can take the system over the “Tipping Point”



Some relevant aspects for terrestrial planets

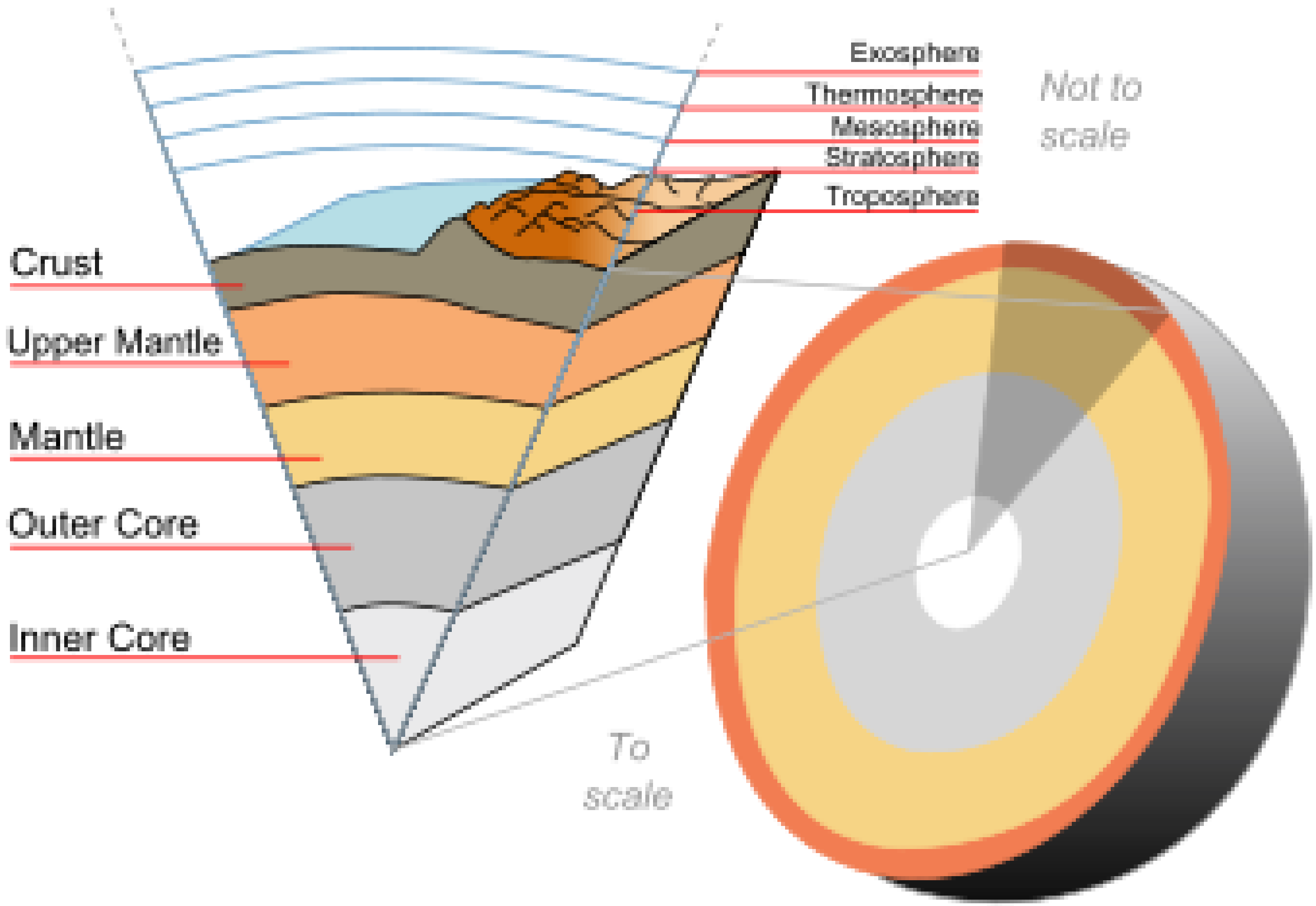
Table 11.1 Atmospheres of the Terrestrial Worlds

World	Composition	Surface Pressure*	Average Surface Temperature	Winds, Weather Patterns	Clouds, Hazes
Mercury	helium, sodium, oxygen	10^{-14} bar	day: 425°C (797°F); night: −175°C (−283°F)	none: too little atmosphere	none
Venus	96% carbon dioxide (CO_2) 3.5% nitrogen (N_2)	90 bars	470°C (878°F)	slow winds, no violent storms, acid rain	sulfuric acid clouds
Earth	77% nitrogen (N_2) 21% oxygen (O_2) 1% argon H_2O (variable)	1 bar	15°C (59°F)	winds, hurricanes	H_2O clouds, pollution
Moon	helium, sodium, argon	10^{-14} bar	day: 125°C (257°F); night: −175°C (−283°F)	none: too little atmosphere	none
Mars	95% carbon dioxide (CO_2) 2.7% nitrogen (N_2) 1.6% argon	0.007 bar	−50°C (−58°F)	winds, dust storms	H_2O and CO_2 clouds, dust

*1 bar ≈ the pressure at sea level on Earth.

Note the relevance of clouds, weather in general and atmospheric composition. Two other very important features to be discussed later are the magnetic nature of the cores and the presence of water in controlling atmospheric carbon dioxide levels .

The core composition of the Earth might be a deciding feature for stabilising the environment

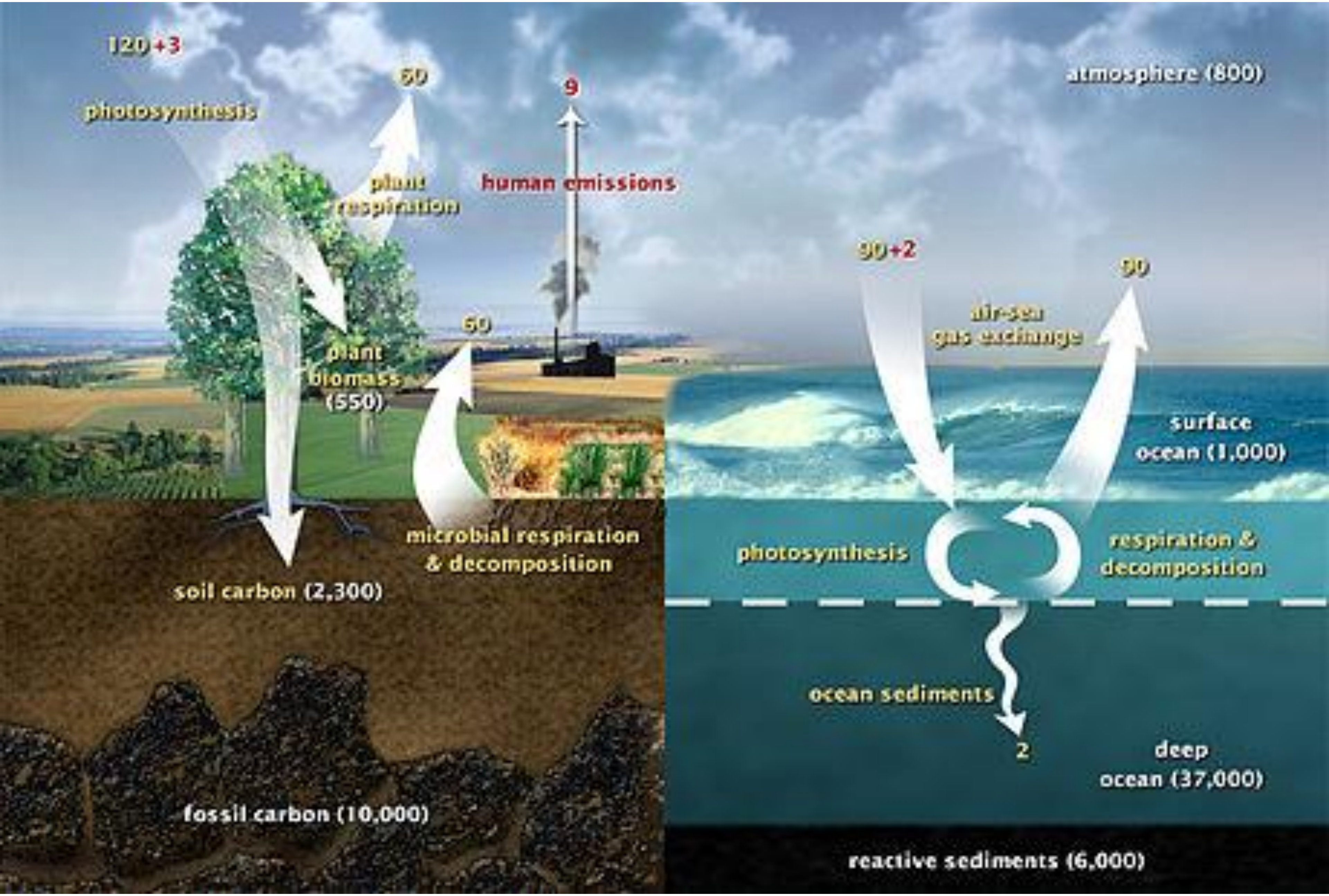


The magnetic core is important for protecting the surface from harmful solar wind - gamma and higher radiation – whilst the protective ozone layer blocks out the lower energy, but harmful to life, uv radiation

Perhaps the main problems lie in upsetting the natural biogeochemical cycling of CO_2

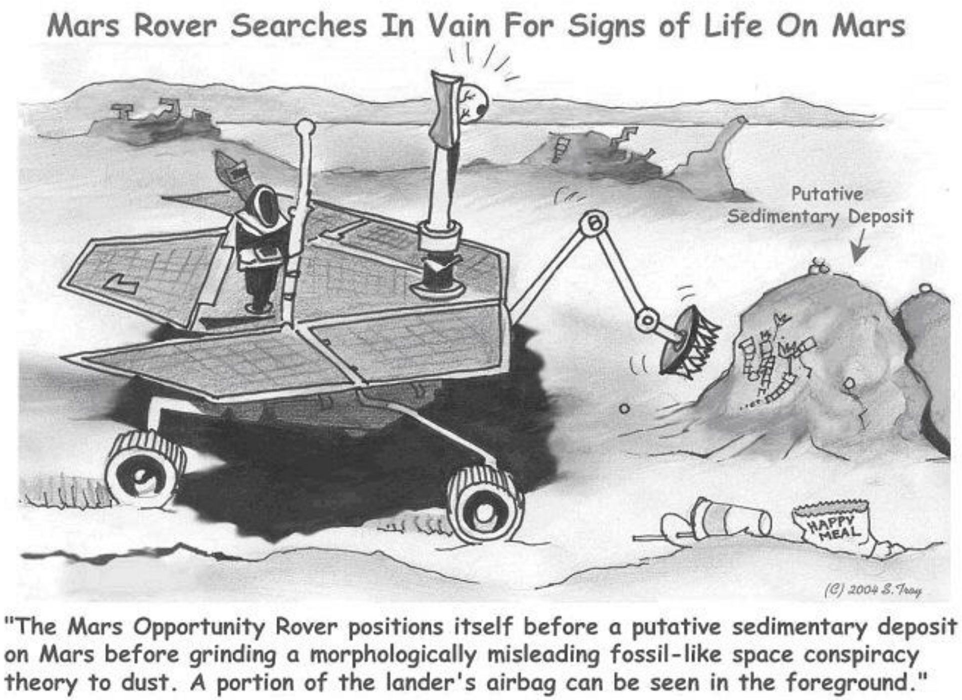
- Why is there so little CO_2 in the Earth's atmosphere compared with the levels on Venus and Mars?
- What trapped the water on Mars and Venus?
- Why is there so little nitrogen on Venus and Mars?
- Why does the Earth have a magnetic core?
- Did all the oxygen on Earth come from photosynthesis?
- Why is seawater a metastable solution?
- Why are rivers not salty?

The CO_2 Cycle



Important to contrast the land and marine interfaces for cycling of CO_2

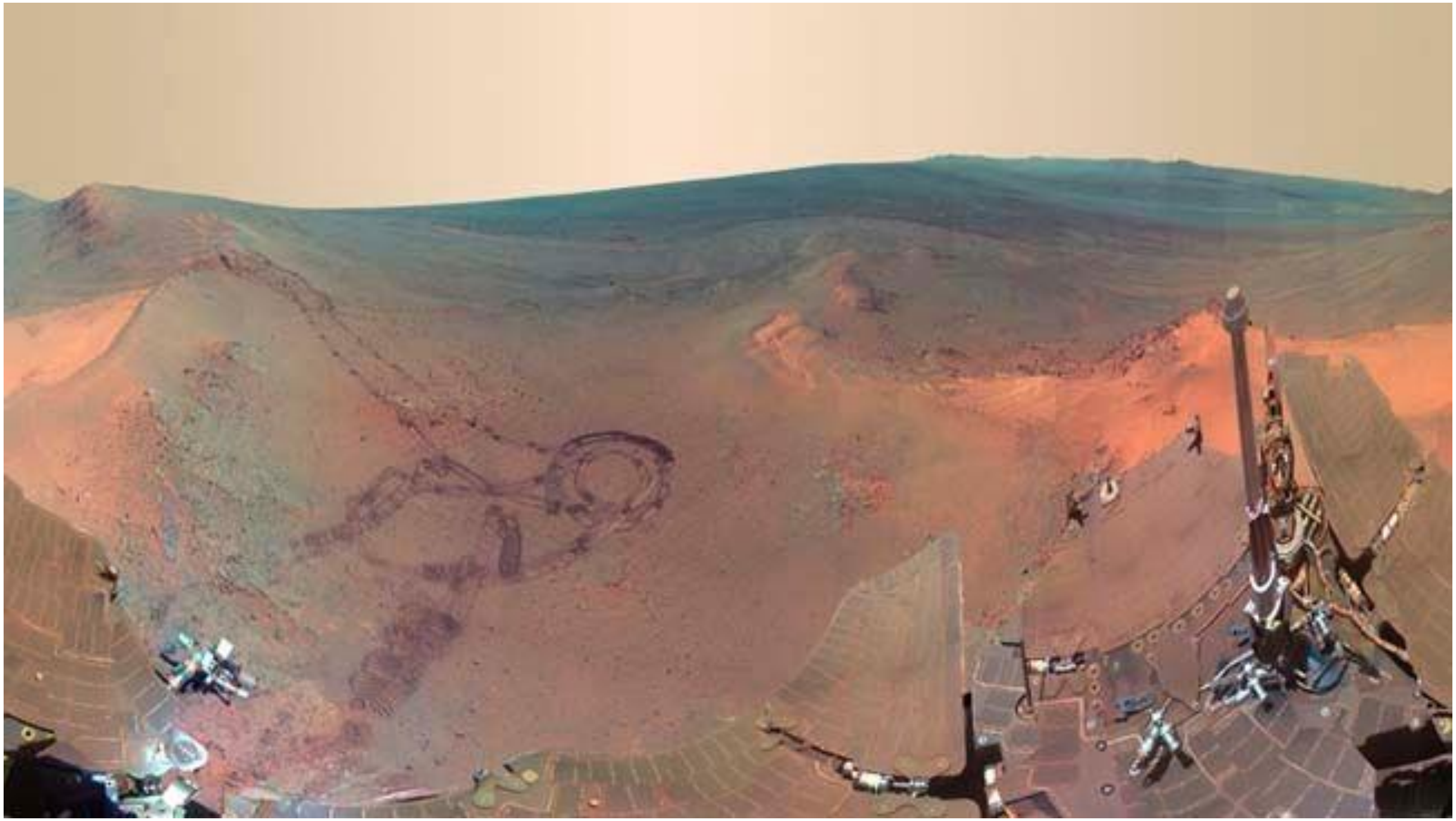
Is there life to be found on Mars?

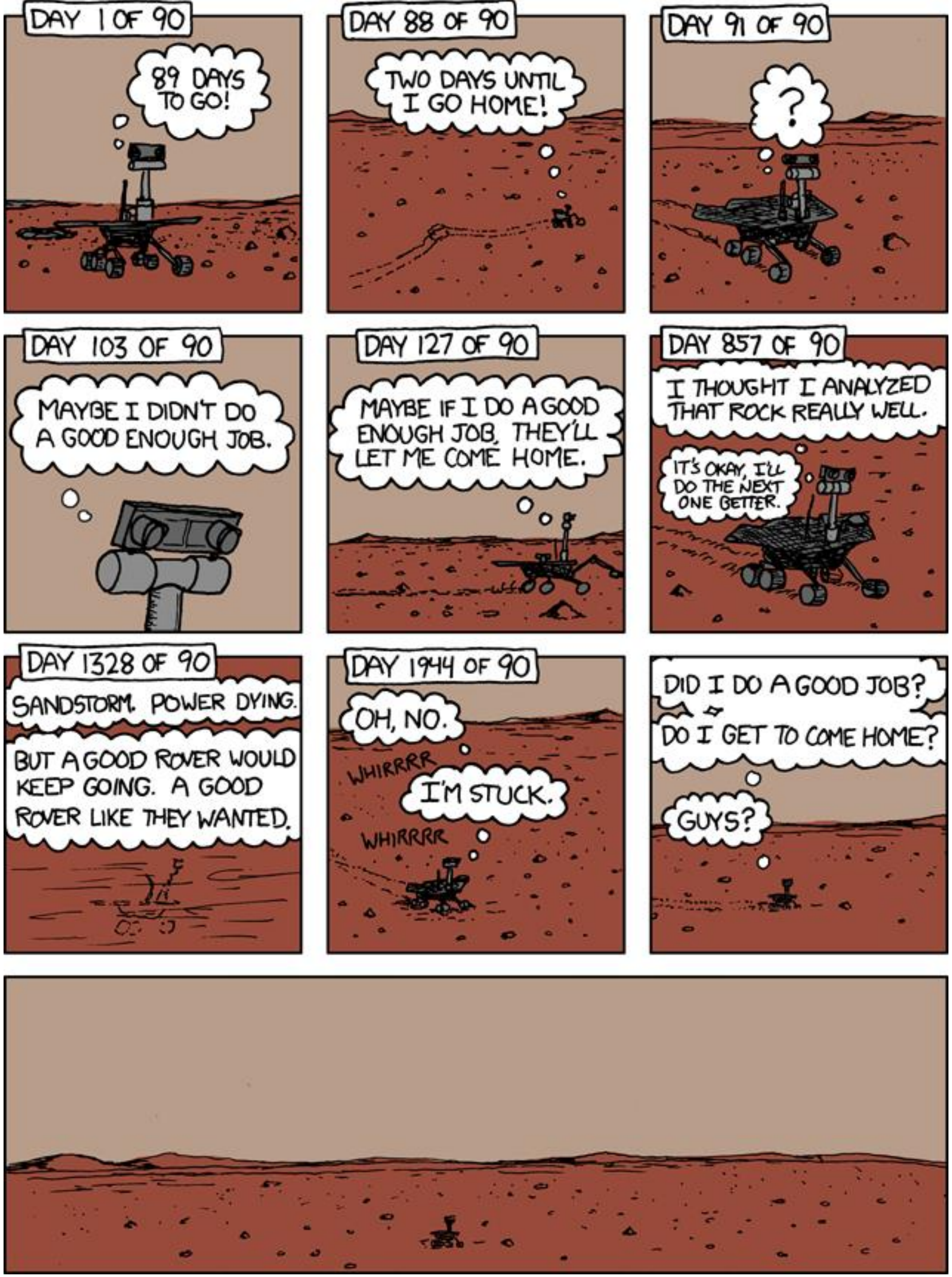


The views from NASA/USA….

The moral: you have to know how to do the measurements and look in the right places… and don't be fooled!

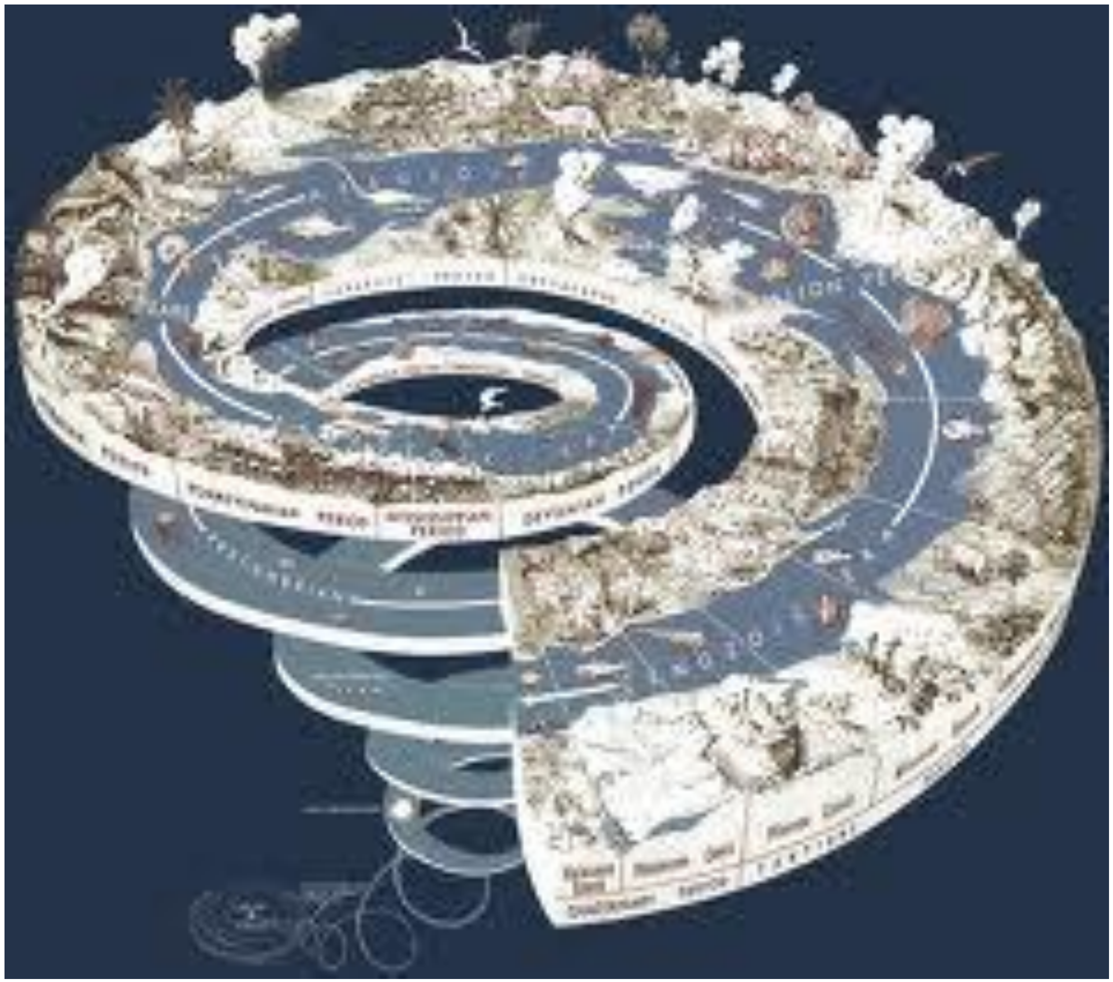
Mount Sharp in the Gale Crater, Mars





The fate of the first and very faithful Mars Rover…

Biogeochemical cycles –3. Geological, Chemical and Biological Evolution on Earth

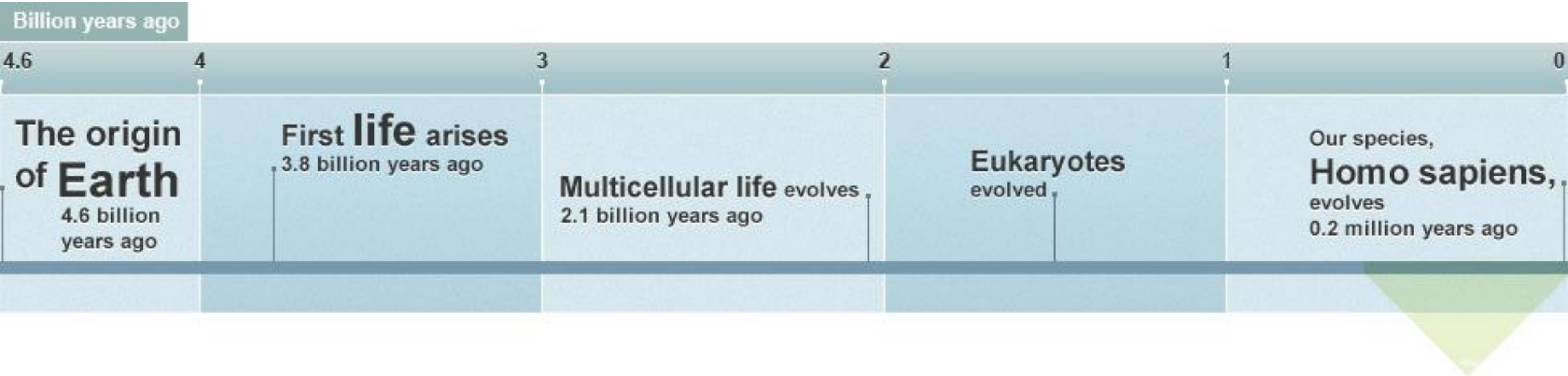


Earth Timeline

The Earth "solidified" about 4.6 billion years ago with the first life probably emerging about 3.8 billion years ago.

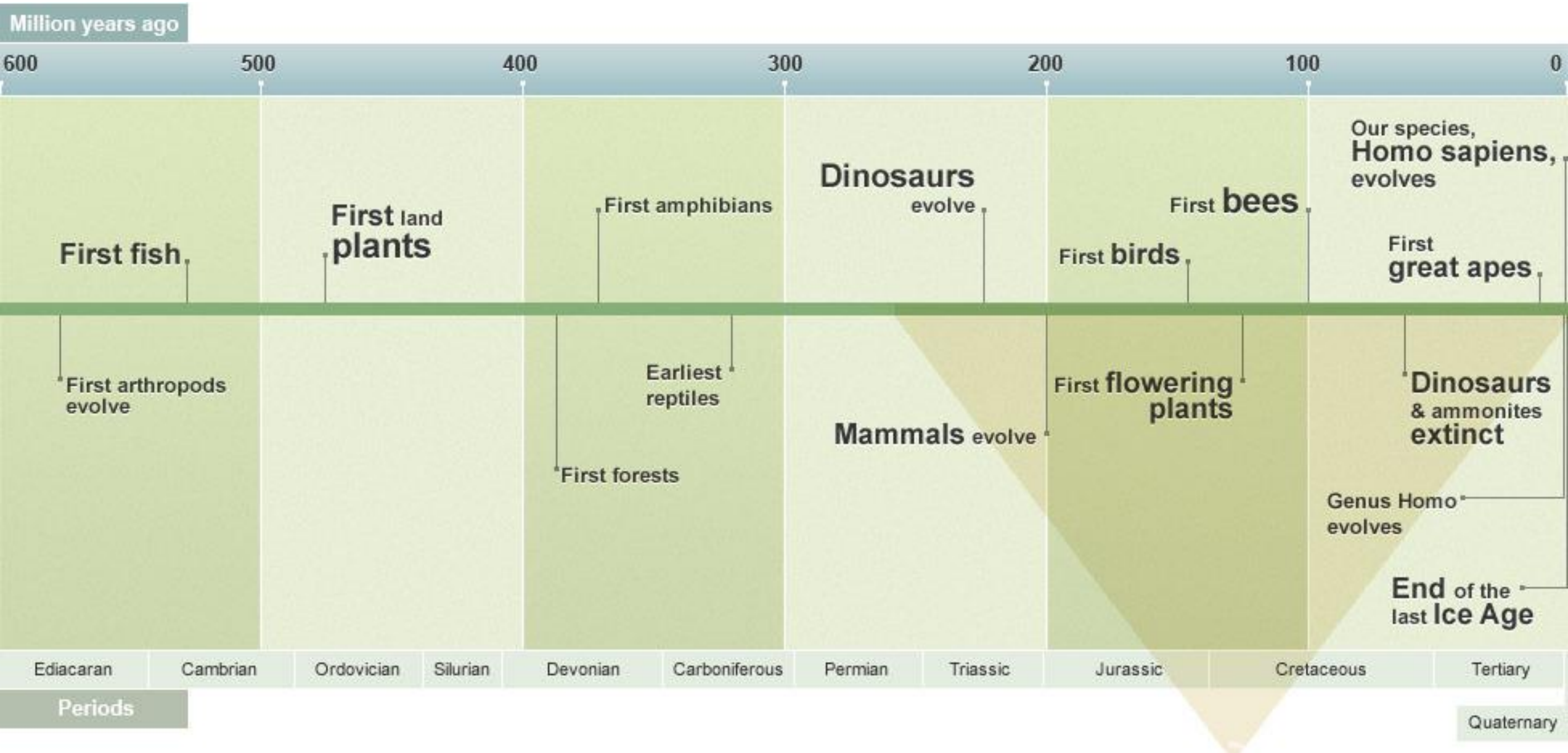
About 1.7 billion years later the first multicellular life forms emerged – after Photosynthesis became a dominant feature on the planet.

Only very recently did the creatures we consider as "part of the fossil record" - i.e. remains to be found in rocks within our geological classification - appear.



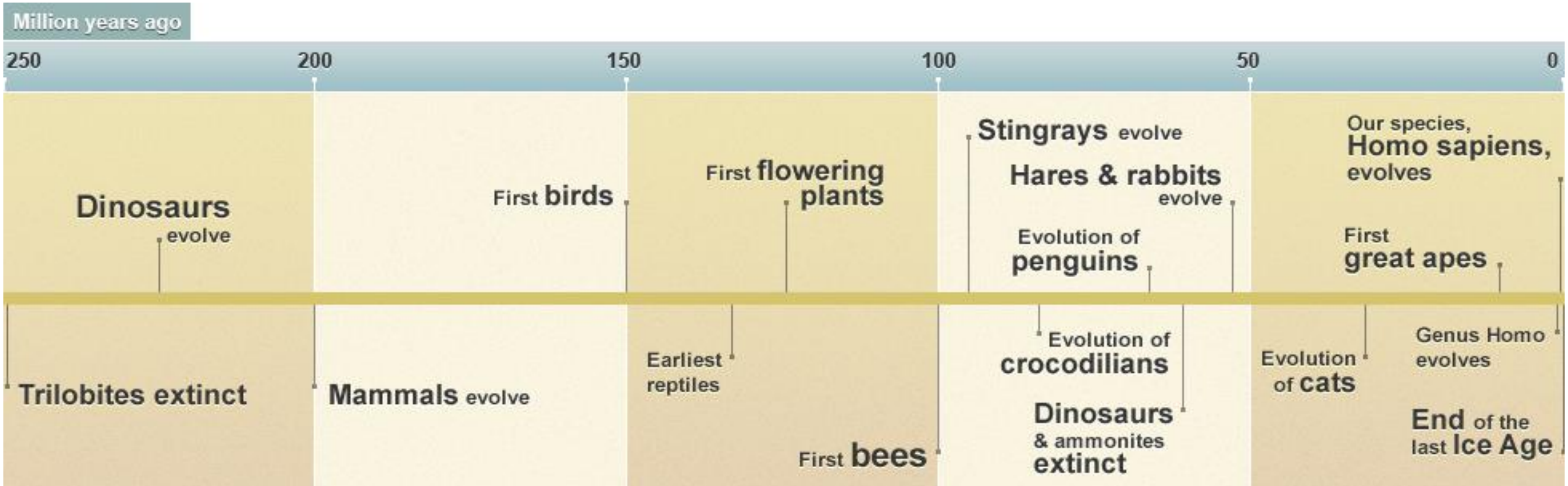
Enlarge this to show Biological Timeline of the fossil record

Timeline of biology in geological context



Enlarge this section to show recent biological timeline

Recent biological timeline



Note that although Homo Sapiens is a very recent addition to the picture, this species has managed to create a very large footprint on the planet.

In the past mass extinctions were caused by naturally occurring catastrophes such as rapid heating (desert Earth) or cooling (snowball Earth) or asteroid hits.

There is a real possibility that Humans will distinguish themselves as the first species to instigate mass extinctions of other species on the planet.

And all the time, this will be monitored, measured and evaluated!

Section though Earth showing the Tectonic Plates floating on the Mantle

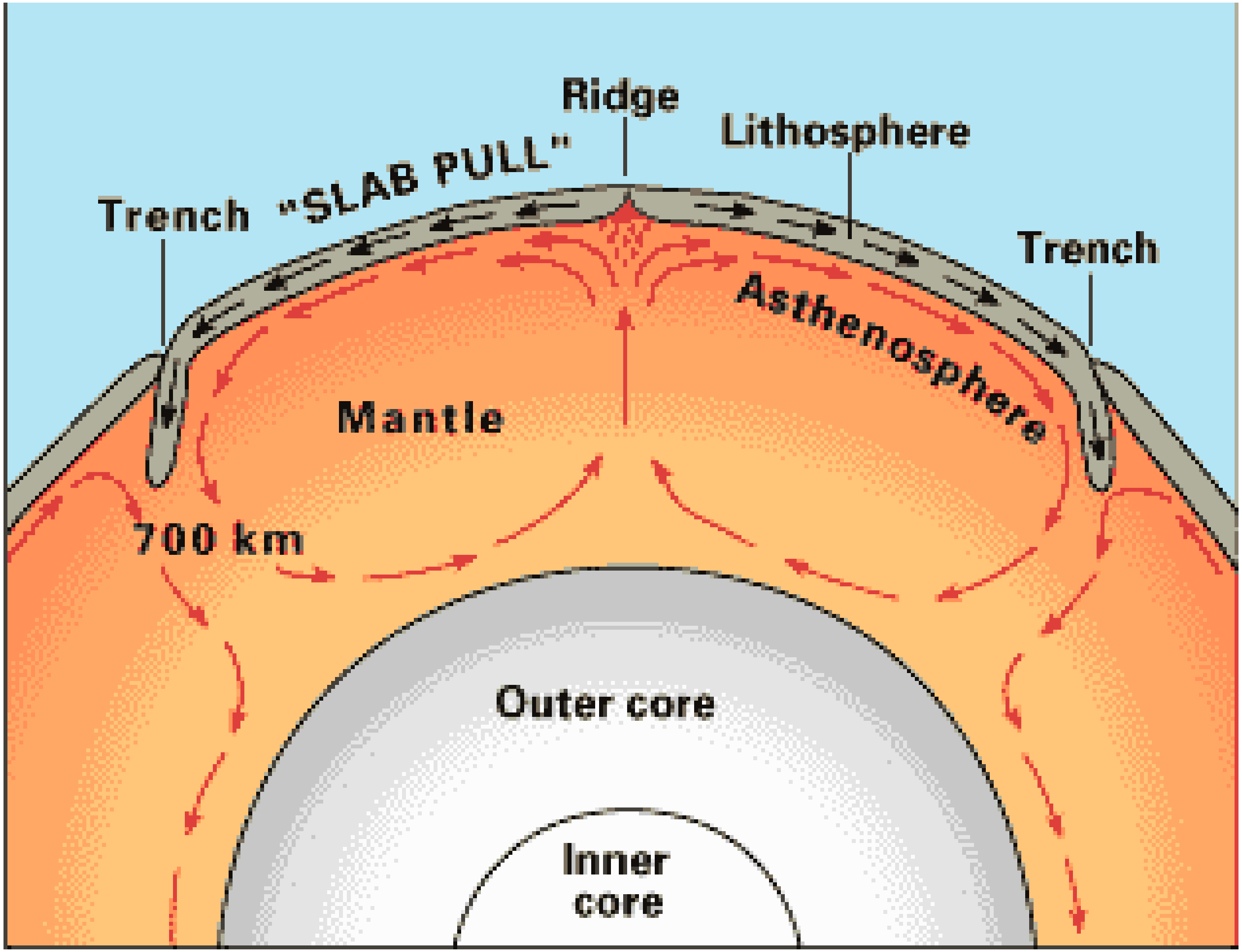
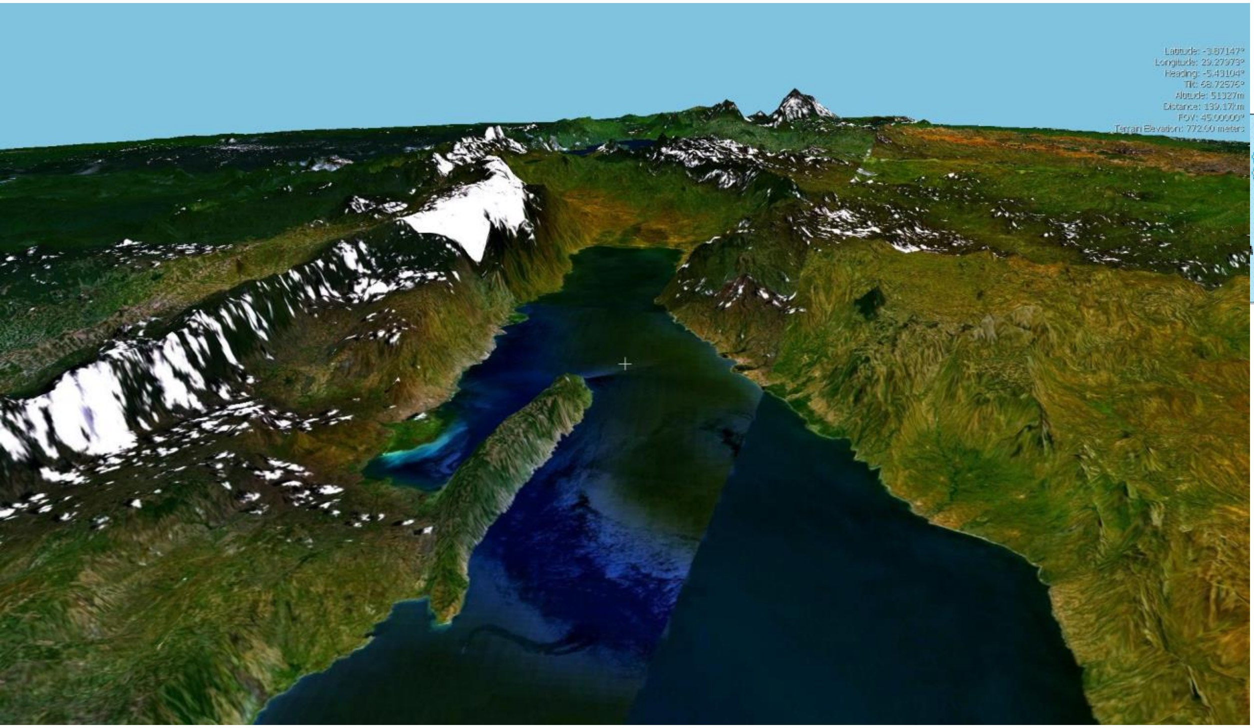


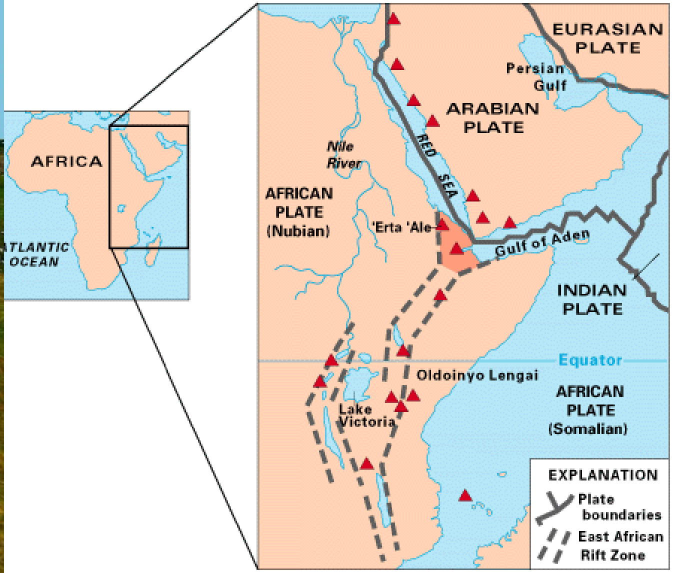
Plate tectonics

- The outermost shell of the Earth - the lithosphere - is tessellated with about twenty giant slabs of rock known as "Tectonic Plates" since they produce the structure on the surface (Greek: *tektonikos* belonging to carpentry, from *tektōn* a builder).
- These plates can move relative to each other at speeds of centimetres per year - approximately the rate at which human fingernails grow.
- The plates slide about on the layer of hotter, softer mantle.
- The mantle is like a supercooled liquid – i.e. a glass.
- Where plates encounter each other, stresses and strains build up manifested in extreme cases by violent earth movements – earthquakes.
- The boundaries of the plates are marked by geological faults although these can occur at some distance from the actual edges just like having a ruck in a carpet which becomes worn.
- Near plate boundaries, molten magma can rise to the surface and erupt to form volcanoes .
- Two types of boundary exist between plates: divergent and convergent.

Divergent boundaries

- The process of adjacent plates moving away from each other is best seen at the oceanic spreading ridges.
- New crust spews out from extensive oceanic ridge systems, like the one seen in the middle of the Atlantic Ocean.
- Smaller scale systems can be seen in rift valleys, such as the African Great Rift Valley (below), Rhine Rift Valley and Scottish Rift Valley.





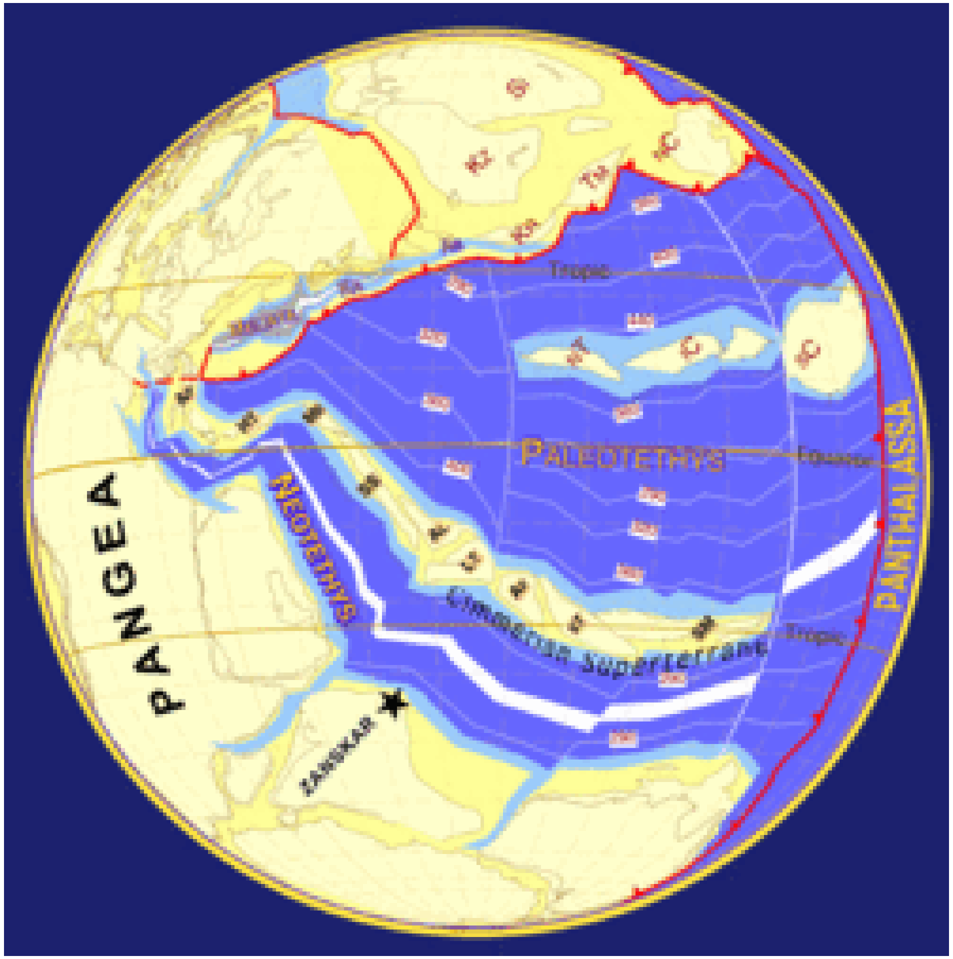
Convergent boundaries

- When two plates meet, a convergent plate boundary forms.
- Usually one plate will slide underneath the other - this will cause some mountain building and lots of volcanic activity - The Andes mountains in Chile are a classic example of this.
- Sometimes plates will collide and one does not flow smoothly under the other giving rise to extensive and rapid mountain building. The Himalayans are an example of this.

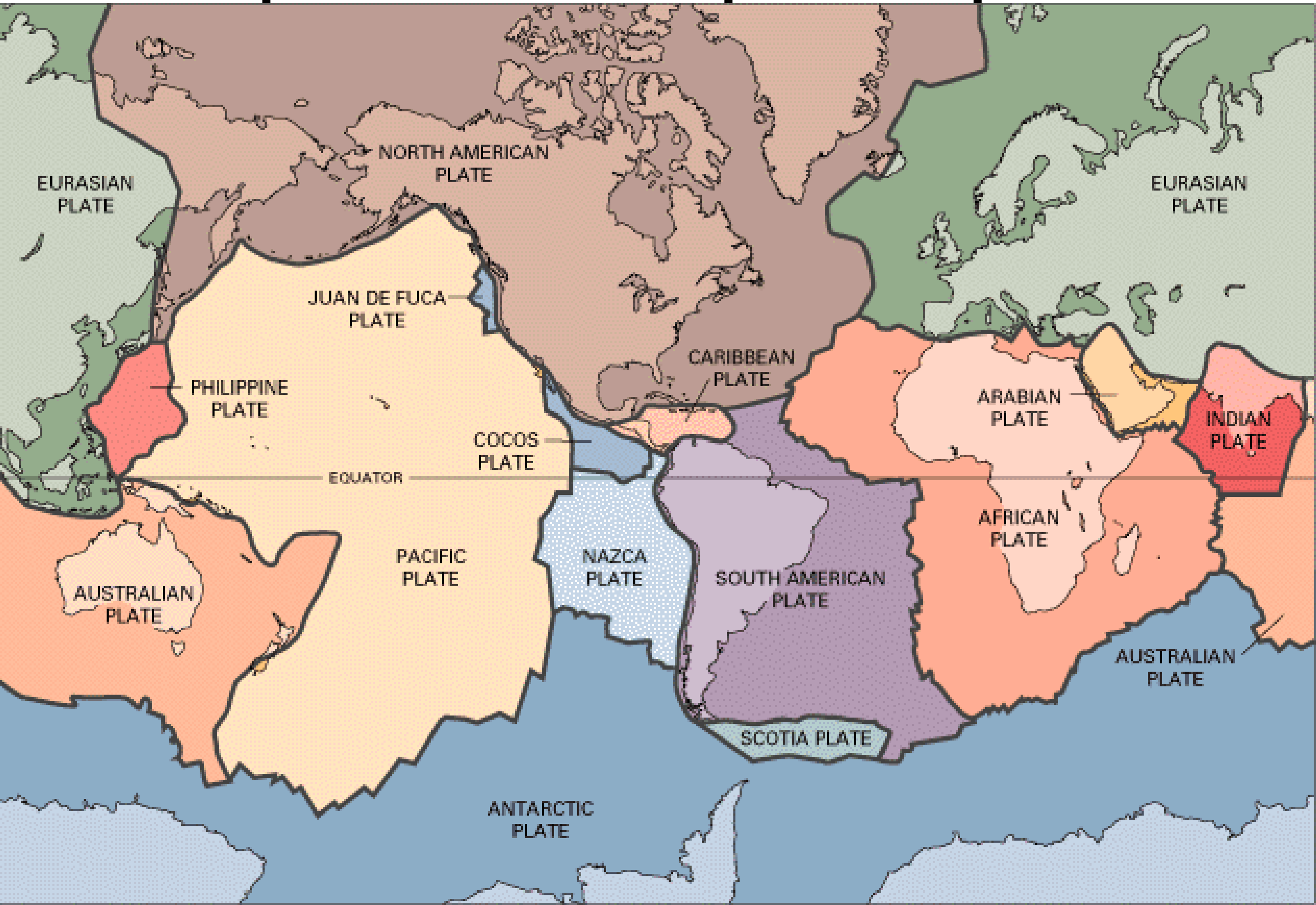
Mount Pinatubo in the Andes showing volcanic activity

The Himalayas

Older mountain building periods and rift valley formation (e.g. Scotland and the Rhine Valley) were in progress when the continental plates started their more recent moves



A map of the tectonic plates at present



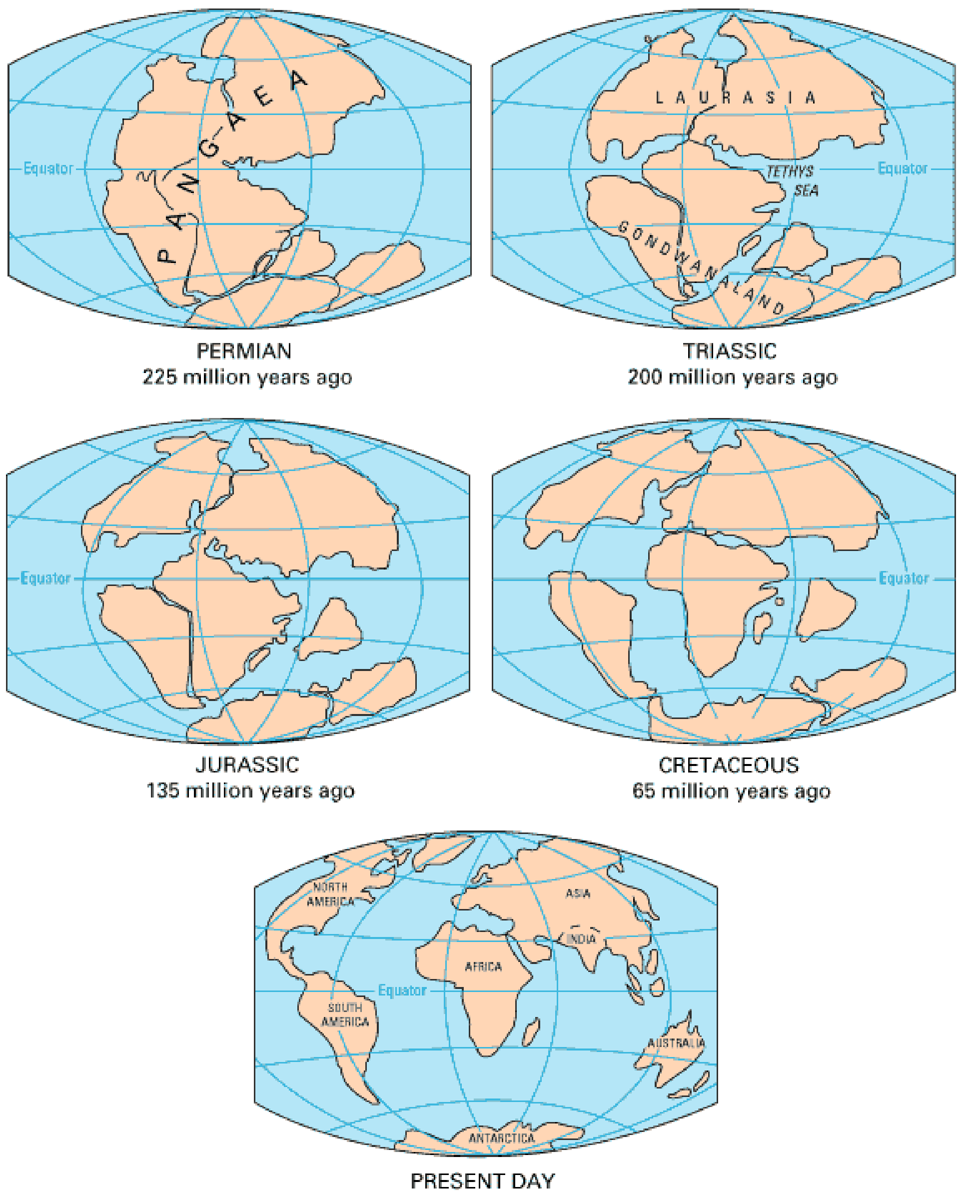
Tectonic plates influence environmental factors

- The plates which form the terrestrial land masses have drifted together and apart many times in the history of life on earth.
- Climate is tied to the position of the plates.
- Plate location determines:
  - ocean currents
  - heat flow
  - salinity
  - oxygen levels
  - glaciation
- Migration is possible if the plates are close together – as for Europe when there was a land-bridge between the British Isles and the European Continent allowing plants, animals and insects to move freely between the two.
- Isolation is possible if the plates are far apart – this is seen in the case of New Zealand which has a unique native Flora and Fauna.

Position of Plates in Recent History

The top four views cover the period when dinosaurs were present – they died out during the Cretaceous period.

It is not known where the plate were before the supercontinent Pangaea existed.



Notice that there is a greater density of plates in the Northern Hemisphere. Recent work predicts that the position of the poles of the Earth's magnetic field might be indicated by plate movement.

Pinatubo ash plume

Origin of the atmosphere and hydrosphere

- The formation of an atmosphere on a planet is important for the subsequent evolution of chemistry and thus potentially biology.
- Volatile gases were either associated with the Earth during its formation or they arrived through meteorite collisions.
- The volatiles were released during the many incidences of heating and melting of the crust. This process is know as outgassing; most outgassing occurred within the first 1 billion years of the Earth's history, although it still takes place through seismic and volcanic activity.
- The primitive atmosphere was probably rich in CO_2, N_2, with lesser amounts of CO, H_2, HCl and traces of NH_3 and CH_4.
- There was probably no O_2 present in the early atmosphere.
- Any O_2 outgassed would have reacted with the metals of the crust to give stable oxides.
- This lack of O_2 is probably the reason why it was easy to form organic molecules without complicated synthetic procedures we often use today.

How did life on Earth evolve?

- The big question is how life actually got going on Earth?
- So far, we don't really know, but chemical experiments show that it is possible to produce the "building blocks for life" (organic molecules).
- Biology takes these building blocks and polymerises them into amazingly complex and precise structures.
- Once a few of these macromolecular scaffolds exist, the Biology can run itself – so the initial formation of the building blocks is like the "firelighter" for any fire – once the fire is going it can be virtually impossible to put out.
- This latter point has been proved over time by the way life still persists in spite of mass extinctions.

The signature of Life

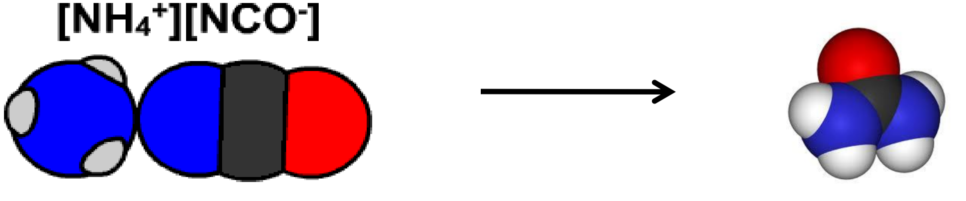
- **What is life?** Difficult to define, but some characteristics are:
- **Order** Living organisms partition resources and nutrients within their systems. This is an energy-requiring process which must be maintained for life to continue.
- **Reproduction** Organisms reproduce their own kind. Life only comes from life.
- **Growth and Development** Heritable characteristics direct the pattern of growth and development producing an organism that clearly belongs to its species.
- **Energy Utilization** Organisms take in energy and transform it to do work. Almost all of life's functions require energy.
- **Homeostasis** Regulatory mechanisms maintain an organism's internal environment within tolerable limits, even though the external environment may fluctuate. This process is known as homeostasis.
- **Evolutionary Adaptation** Life evolves as a result of the interaction between organisms and their environment. As the environment is rarely stable, life must adapt to survive in these new living conditions.

Chemical origins of life on Earth

- Experiments concerning the origin of life should take a few important points into consideration.
- How were small organic molecules (amino acids, nucleic acids, lipids) formed in the primitive earth environment?
- How were these small organic molecules joined together to form polymers (long chains of organic molecules)?
- How were abiotically produced molecules segregated to give droplets (protobionts) with chemical compositions different from their surroundings?
- What was the origin of heredity?
    - We will not attempt to answer all of these questions!

History of organic synthesis from inorganic compounds

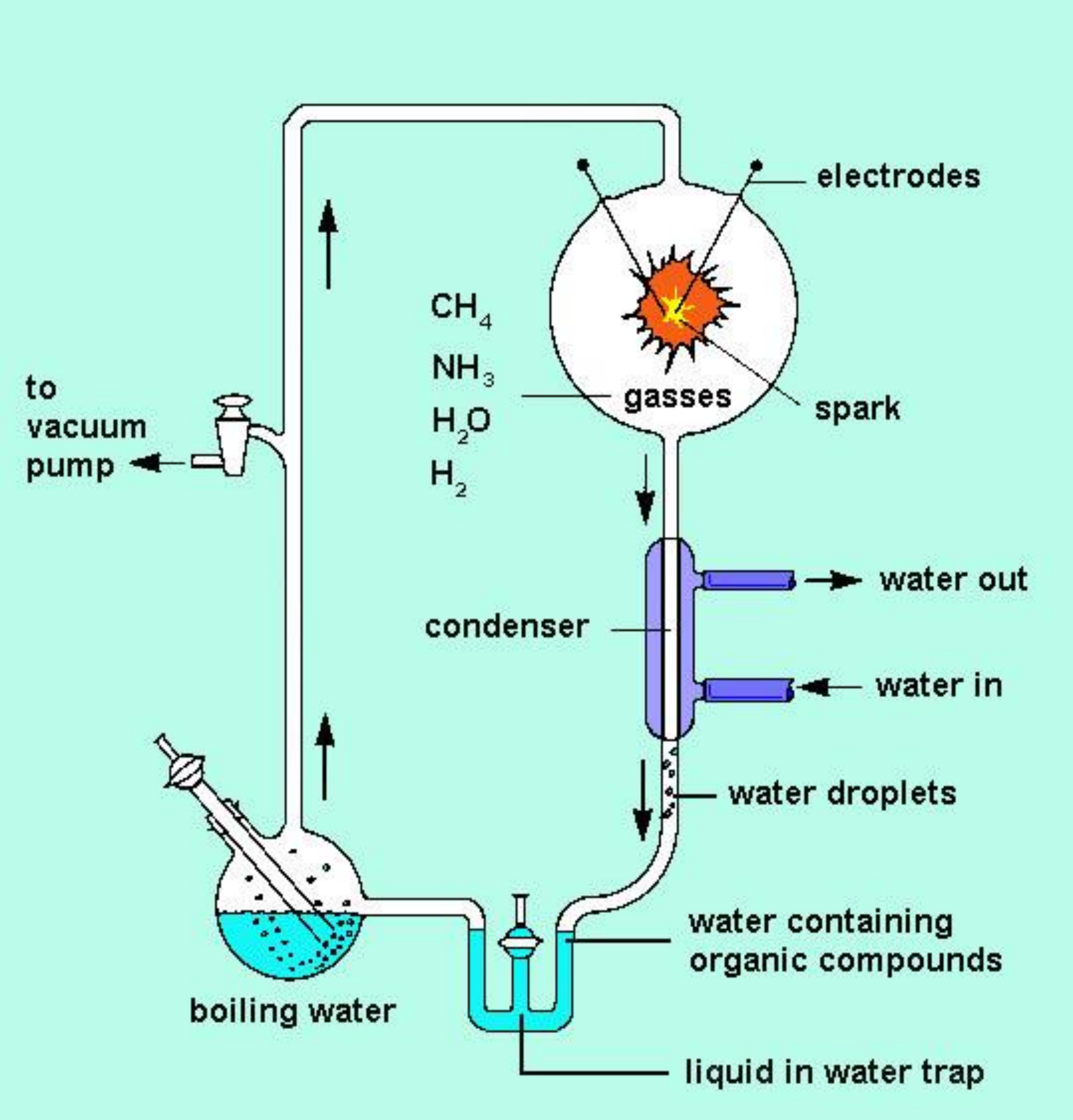
- Famously, in 1828, Fritz Wöhler reported the synthesis of the organic molecule urea starting from a purely inorganic compound.
- The **Wöhler synthesis** is the conversion of ammonuim cyanate into urea.
- This is considered as the starting point of modern organic chemistry, since previously it was believed that organic compounds could only be obtained from living (or ex-living) systems. This view was known as “Vitalism”.
- Urea was discovered in 1799 and previously could only be obtained from biological sources such as urine.
- In the reaction ammonium cyanate first decomposes to ammonia and cyanic acid and these then produce urea via a nucleophilic addition with subsequent tautomerisation.
- Overall reaction is: $NH_4(NCO) \longrightarrow NH_3 + HNCO \longrightarrow (NH_2)_2CO$



A famous experiment with the primordial soup

- In 1953, Stanley Miller and Harold Urey used an apparatus (basically a still) to recreate what is proposed to be the primitive environment of the earth.
- A warmed flask of water simulated the primitive oceans.
- The atmosphere in the Miller-Urey model was composed of H_2O, H_2, CH_4 and NH_3.
- Sparks simulating lightning were discharged into this synthetic atmosphere to mimic lightning.
- A condenser cooled the atmosphere, raining water and any dissolved compounds back into the miniature sea.

The Miller-Urey Experimental Set-Up



Results of Miller-Urey Experiments

- As materials circulated through the apparatus, the solution in the flask changed from clear to murky brown.
- After one week the analysis of the contents of the flask revealed a variety of organic compounds, including amino and nucleic acids thus providing one scenario for the production of organic molecules form simple inorganic precursors.
- The fact that the primitive atmosphere was reducing aided in preventing oxidation of the precursors.
- A reducing environment may also help in the formation of polymeric species.
- The addition of clays into apparatus similar to that used by Miller and Urey can generate polymers.
- The metal ions on the clays probably act as catalysts or templates for the formation of polymers.

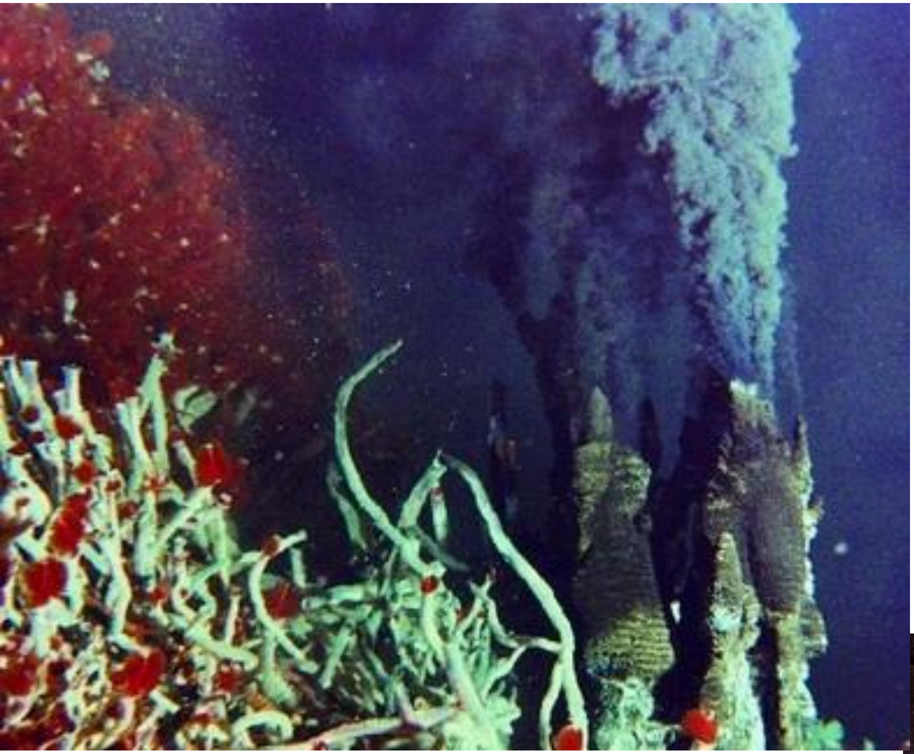
RNA world

- The **RNA world hypothesis** proposes that self-replicating ribonucleic acid (RNA) molecules were precursors to current life which uses deoxyribonulceic acid to replicate proteins and RNA as a messenger.
- RNA is able both to store genetic information, like DNA, and to catalyse chemical reactions as an enzyme (protein) can.
- The suggestion is that it may have played a major step in the evolution of life.
- RNA can be produced in “primordial soup” experiments similar to those of Miller and Urey.

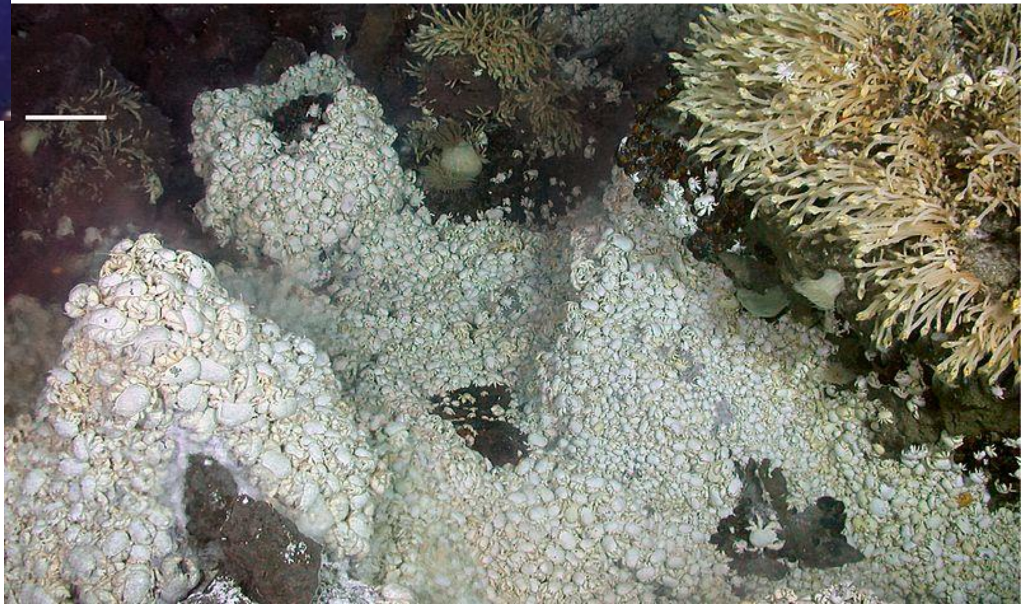
Wächtershauser's theory about the black and white smokers

- This idea links to the suggestion that hydrothermal vents provide a 'reactor' for RNA as explained in the RNA World hypothesis.
- Hydrothermal vents, the black and white smokers, rely on chemical energy from geothermal vents to sustain a complex range of organisms.
- Swarms of bacteria thrive in this environment which acts as an interface between the high temperature vents and cold oxygenated sea water. The bacteria thrive on gases produced by the vents such as methane and use these chemicals to produce simple organic molecules to support the local ecosystem in a similar way to plants using photosynthesis.
- Wächtershauser has proposed that a biochemical cycle grew and assembled the first living cell.
- In this scenario, the chemical coupling of an iron salt and hydrogen sulfide from the hydrothermal vents produced pyrite (FeS_2).
- Simple molecules, such as CO, organic acids and sugars, gather on the surface of the pyrite and are catalysed or templated to produce new molecules. In this way, the system does not use any cellular components and starts from a compound - pyrite - which was abundant in early Earth's oceans.

Black and white smokers as hotbeds for life?

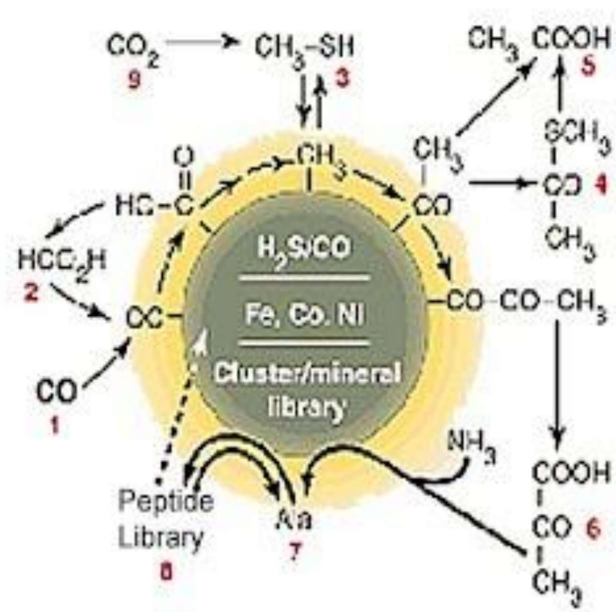


Located 3 kilometers underneath the surface of the Atlantic Ocean, the hottest water ever found on Earth has been found emanating from two black smokers called Two Boats and Sisters Peak. So hot, in fact peaking at temperatures around 450 ^{o}C, that the fluid has moved from being a fluid to being a supercritical fluid



The environment becomes rich in nutrients for other creatures to enjoy a feast (crabs in right picture)

An iron pyrite particle as a template or catalytic surface for the formation of biologically relevant organic molecules



Other thoughts on the origin of life

- Pyrite has been the focus of theories regarding the origin of life since it was first suggested by Wächtershauser in1988.
- These reactions would take place around hydrothermal vents.
- Another possible birthplace may be at the interface between land and sea.
- Charles Darwin suggested life might have originated "in some warm little pond with all sorts of ammonia and phosphoric salts, light, heat electricity etc."
- John Desmond Bernal expanded on this idea, suggesting that life could have begun in tidal regions, where molecules faced alternating wet and dry periods. The wet period would dissolve chemicals and allow them to react with each other, while the dry periods would allow the chemicals to condense, spurring further reactions.
- Although the right combination of chemicals and energy for life's origin could have been present at hydrothermal vents, as Wächtershauser suggests, sceptics say that such a hot environment would have endangered the formation of delicate proteins and RNA strands.

Waterworlds and life

- The shallow water theory means there would be enough protection form the effects of uv radiation – estimated that the processes should occur a few metres below the surface.
- In the model proposed by Edwards, University of Toronto, it is the electrochemical properties of pyrite which help the “feedstock” species come together.
- Simple substrates such as CO_2 or CO, present in the early atmosphere, are combined with nitrogen containing species on the surface of submerged pyrite particles to produce amino acids etc.
- When pyrite absorbs sunlight, a weak electrical current is generated. In the Earth’s early anoxic environment, this effect would have been further enhanced – remember the details of the electrochemical series.
- This photoelectric quality could have led to carbon and nitrogen fixation. A primitive metabolism would then have developed around these fixation sites. Edwards suggests that this process would have been very fast, occurring in a few weeks or less.

Getting life going

- The inspiration for this theory was the work of Helmut Tributsch at the Hahn-Meitner Institute in Berlin who was working on using pyrite in solar cells.
- Tributsch became involved and tested different samples of pyrite and also discovered that the amino acid cysteine would have played a vital role in life's origin, because cysteine is able to deliver the chemical energy contained in pyrite in a form that can be utilised by primitive organisms.
- For example, *acidothiobacillus ferrooxidan* uses cysteine to dissolve pyrite in order to acquire iron and sulfur.
- *Leptospirillum ferrooxidans* induces electrochemical corrosion on pyrite to recover iron.
- Although these organisms do not use light-driven reactions, the use of pyrite in such primitive metabolisms is noteworthy.
- The details of the composition and form of the pyrite mineral also seem to be important.

Solar powered life

- The process of producing food from chemicals is called CHEMOSYNTHESIS.
- It is thought that the earliest life-forms were chemosynthetic, but that PHOTOSYNTHESIS – production of food from sunlight - was not far behind.
- By receiving **energy from the Sun**, pyrite could have set the stage for the origin of photosynthesis. Note that many of the enzymes in modern photosynthetic organisms are metalloproteins involving iron-sulfur clusters.
- A photosynthetic cell harnesses light energy by using two kinds of proteins.
- These are Photosystem I and Photosystem II and we will discuss these in more detail later.
- Early organisms used either Photosystem I or Photosystem II for obtaining energy through (photo)electrochemistry.
- The earliest, non-oxygen producing **photosynthetic** organisms are thought to be purple bacteria, which rely only on Photosystem I for energy.
- Purple bacteria use energy from the sun, but cycle electrons from substances other than water, such as metal ions, and therefore release no oxygen. Most species are strict anaerobes and live in the sediment of ponds and lakes.

Blue-green algae

- So-called blue-green algae became a dominant lifeform on Earth, partly due to their ability to photosynthesise leading to the release of huge amounts of byproduct oxygen into the atmosphere ca 2.4 billion years ago, which effectively killed off most of the anaerobic competition once the oxygen had finished oxidising surface minerals – known as the "Rusting of the Earth".
- Strictly these bacteria should be not be called blue-green algae since algae are Eukaryotes (have a nucleus and organelles) and these bacteria are Prokaryotes (no membrane sheathed organelles and a simple RNA strand at the centre). They were the first photosynthesising prokaryotes to produce oxygen.
- Therefore better to call them cyanobacteria, where cyan is a shade of blue with green notes.

Cyanobacteria and the Great Oxygen Event

Cyanobacteria and the Great Oxygen Event

- Cyanobacteria are also associated with the formation of the stromatolites we saw earlier. They live an aquatic environments and are famous for the poisonous blue-hazes which can affect lakes in hot Summer weather.
- The release of oxygen into the atmosphere 2.4 billion years ago led to a change in the balance of gases and the subsequent dilution of methane resulted in the Huronian glaciation period, lasting until 2.1 billion years ago.
- Quite a big impact from such a small organism – mass extinction and global cooling!
- Cyanobacteria not only produce oxygen – they also fix nitrogen.

Further points about biological evolution

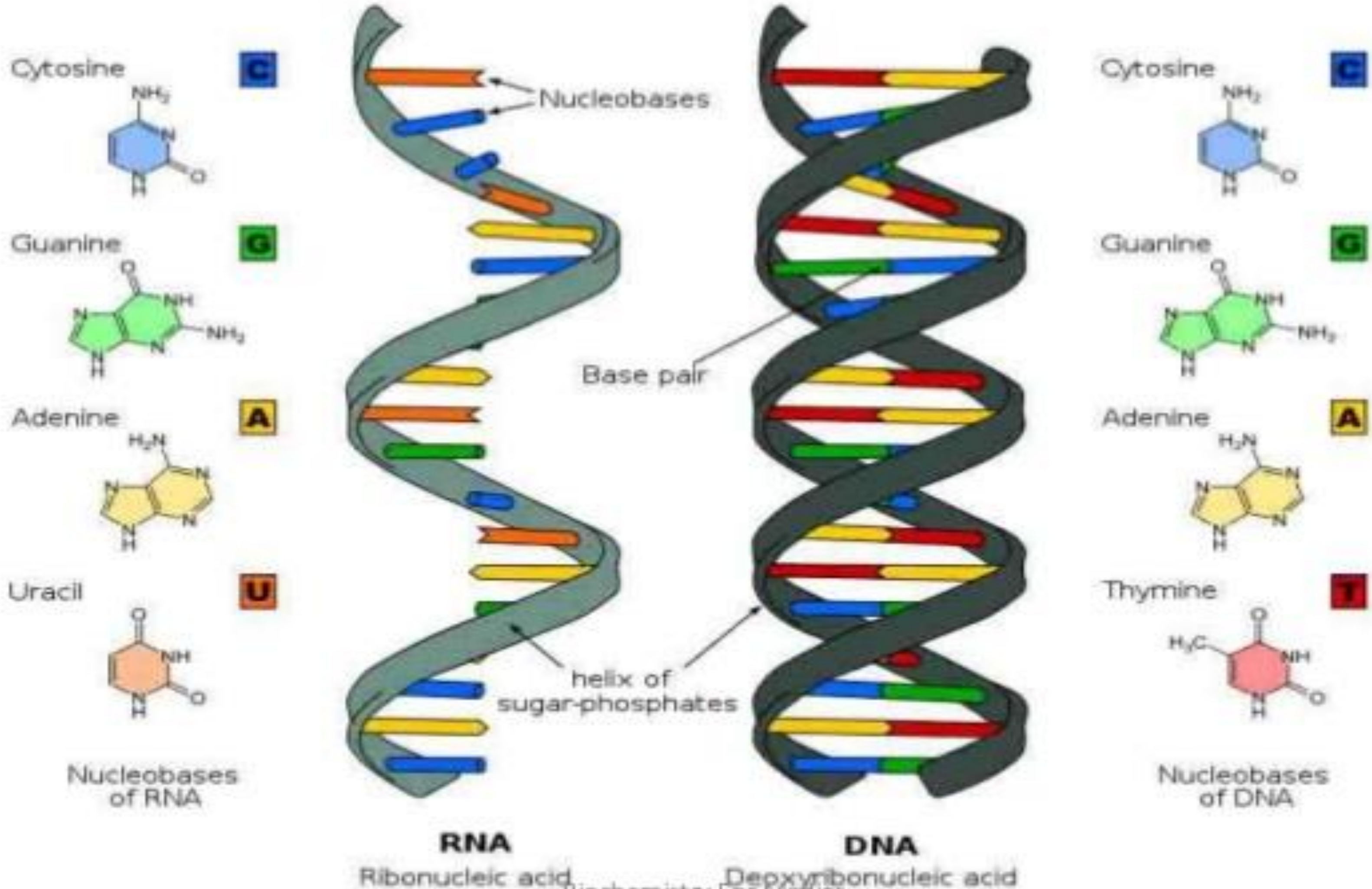
- Other oxygen producing photosynthesisers are eukaryotes. Photosynthesis takes place in chloroplasts.
- Chloroplasts are thought to to derive from cyanobacteria through a process known as endogenesis (also known as symbiogenesis).
- Plastids like chloroplasts are formerly free living prokaryotes taken inside another prokaryote originally about 1.5 billion years ago.
- For more details see the article by Russell J. Garwood:

Patterns in Palaeontology. The first 3 billion years of evolution. Palaeontology online, Vol. 2 Article 11, 1 - 14

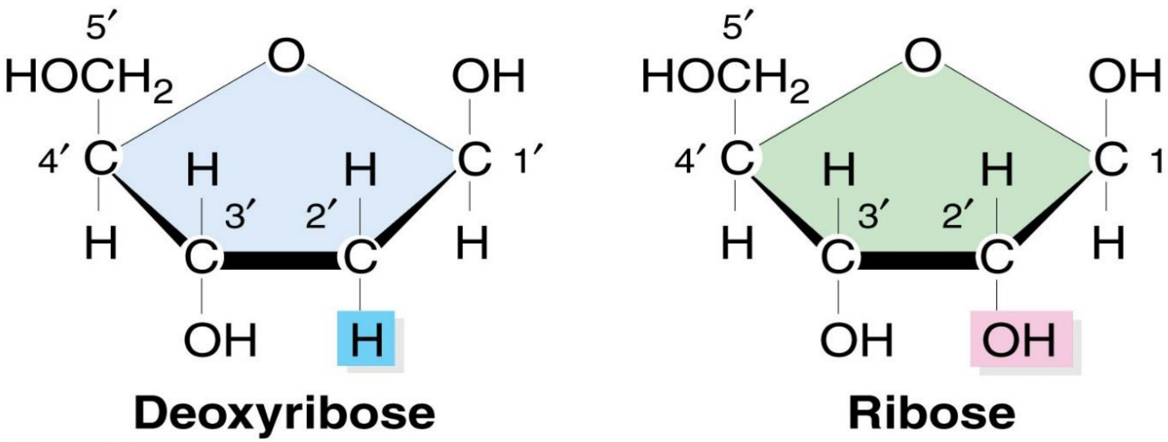
Biogeochemical cycles –4. Important Biomolecules

- The evolution of “synthetic” chemistry on the planet Earth is remarkable.
- In particular, the ability to stabilise relatively weakly connected atoms with what we call chemical bonds has given a huge scope to the development of biology (life).
- Furthermore, relatively weak bonding forces can be used in concert to create remarkably robust structures, including many of the Earth’s creatures.
- We are constantly learning from these examples and developing Chemistry correspondingly.
- The complex nature of biological structures and their finely-tuned energetics can give amazing insights into the future possibilities for “Molecular Chemistry Evolution”.

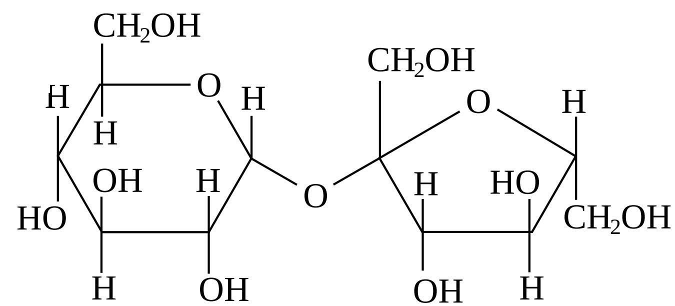
RNA V/S DNA


Cytosine
C
Guanine
G
Adenine
A
Uracil
U
Nucleobases of RNA
Nucleobases
Base pair
helix of sugar-phosphates
Cytosine
C
Guanine
G
Adenine
A
Thymine
T
Nucleobases of DNA
RNA
Ribonucleic acid
DNA
Deoxyribonucleic acid

Sugars



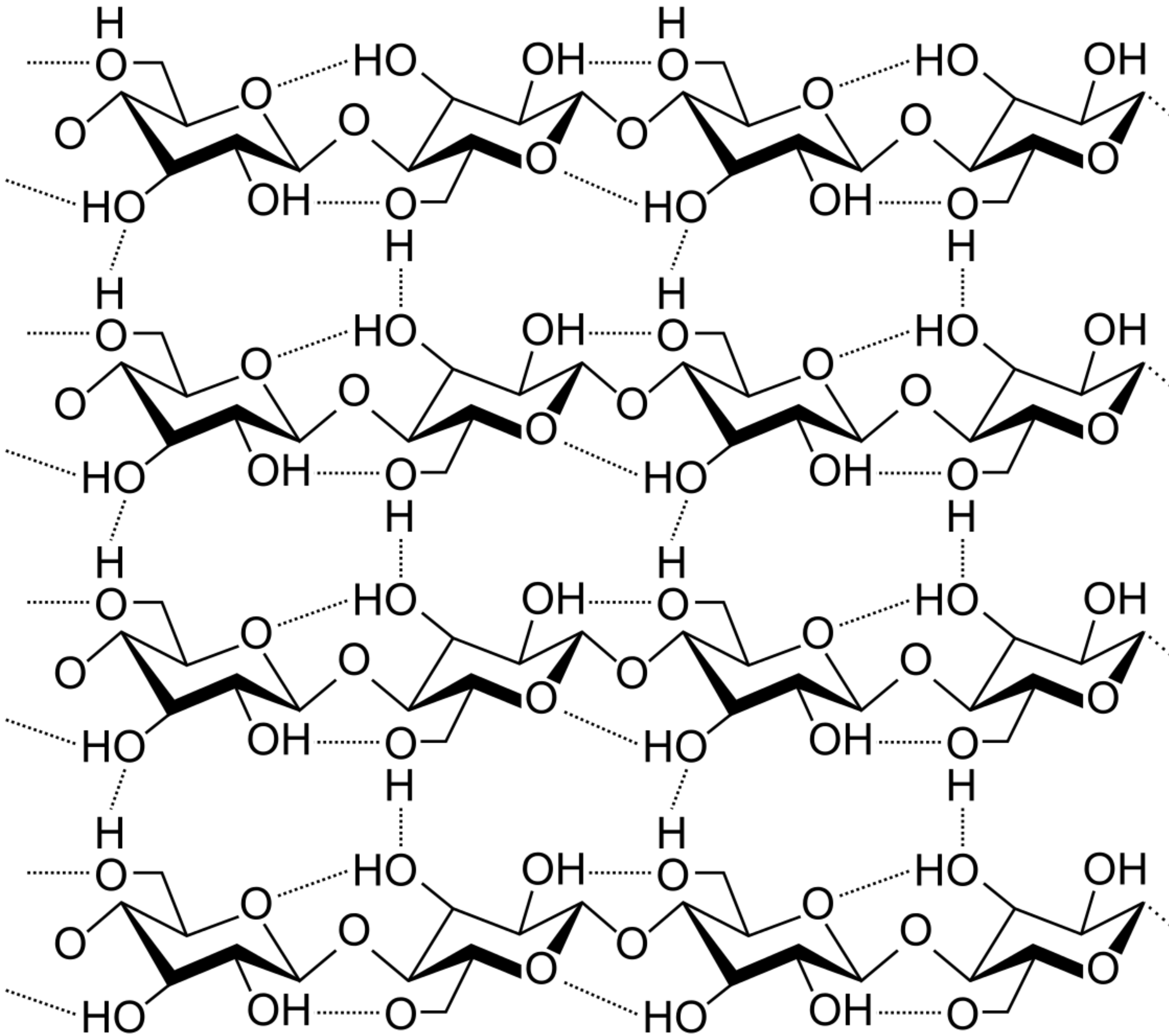
Below: What we use in cooking and baking and derived from sugar cane.



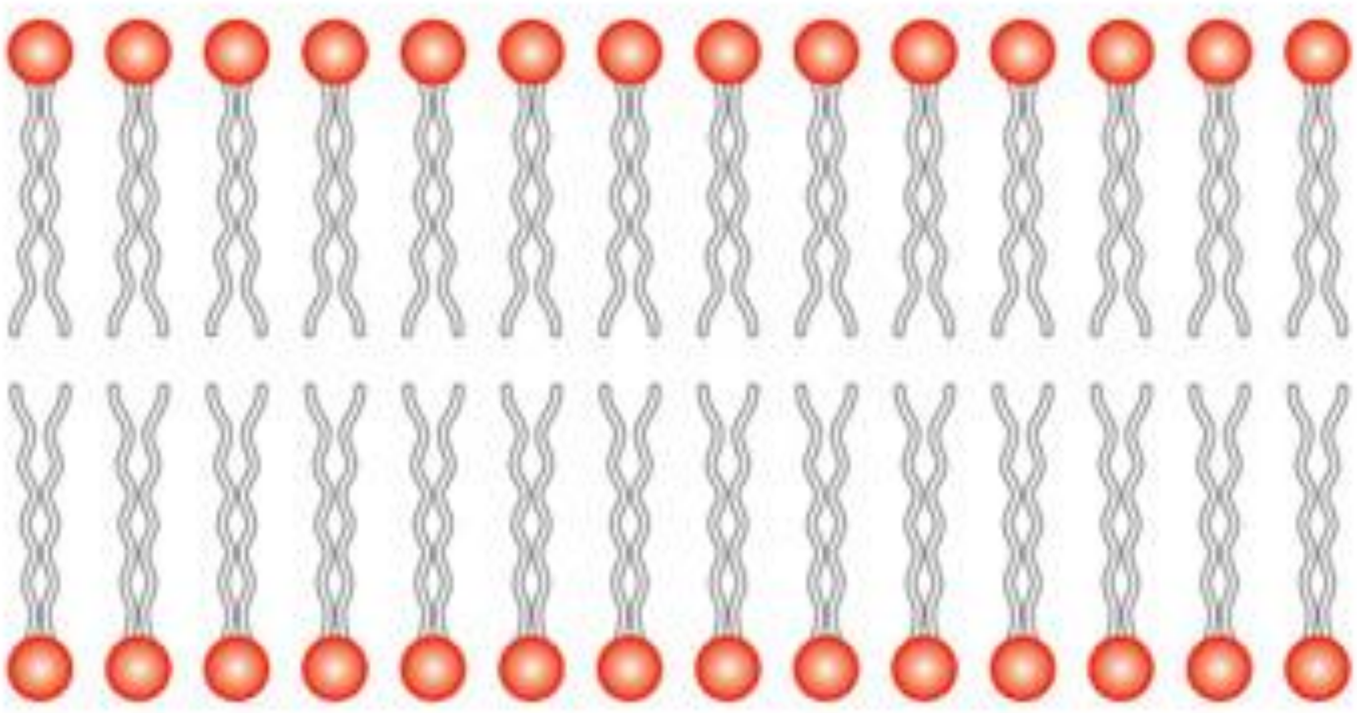
Above: The 5-membered sugar rings (pentoses) **deoxyribose** (a building block for DNA and **ribose** (a building block for RNA).
The deoxygenation of the –OH group highlighted pink in the RNA ribose structure leading to the more stable deoxyribose means that the DNA molecule is much more stable than RNA.

Saccharose, made up of glucose (left, a hexose) and fructose (right, a pentose).

Cellulose – a polymer of glucose and important for plants



Lipid bilayers

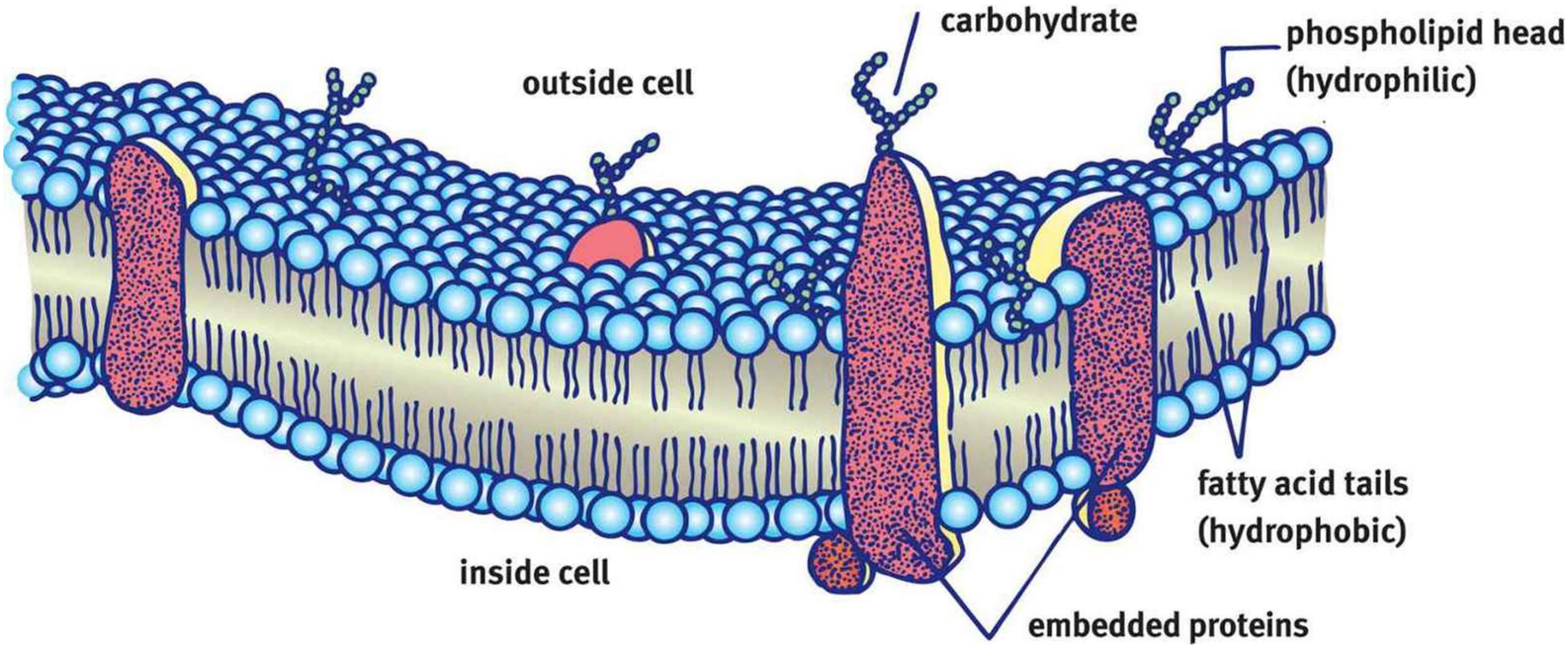


Fatty acids have hydrophilic heads and hydrophobic tails – ideal to separate things from water and create a boundary when in a double layer like this.

Fatty acids are carboxylic or phosphoric acids (the heads) with long carbon chains (the tails).

Lipid bilayers create cell membranes – i.e. walls.

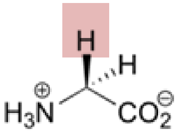
Phospholipid bilayers form cell walls



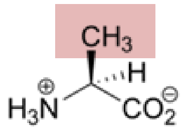
Amino acids and proteins

- Amino acids form the building blocks for proteins.
- They have functional groups at the alpha carbon and there are 20 important versions which are found in organisms.
- The substitution at the carbon leads to the molecules showing chirality (except for glycine) and all amino acids found in organisms twist circularly polarised light to the left and thus designated as L-amino acids. Nearly all are also of the *S* configuration.
- The special nature of the peptide bond means that when two amino acids join together to form a peptide, a certain structural rigidity is built in as manifested when polypetides form to give a protein structure with characteristic structural features.

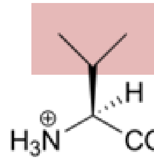
Nonpolar, aliphatic side groups



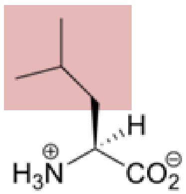
Glycine
Gly, G



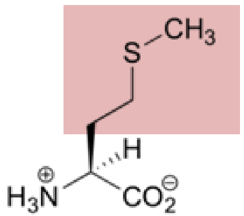
Alanine
Ala, A



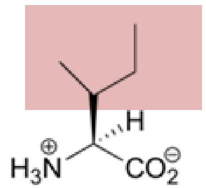
Valine
Val, V



Leucine
Leu, L

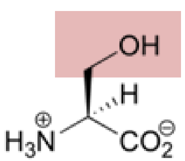


Methionine
Met, M

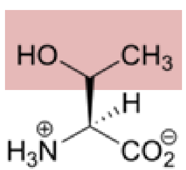


Isoleucine
Ile, I

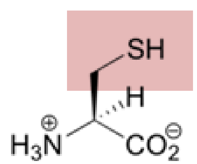
Polar, uncharged side groups



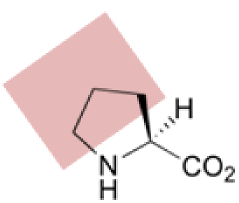
Serine
Ser, S



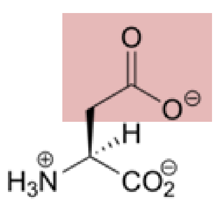
Threonine
Thr, T



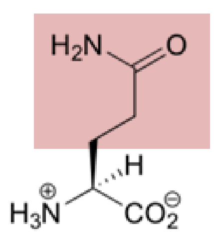
Cysteine
Cys, C



Proline
Pro, P

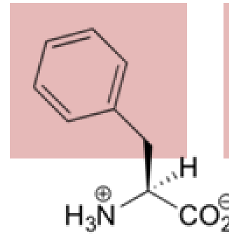


Aspartate
Asp, D

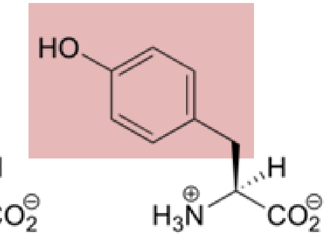


Glutamine
Gln, Q

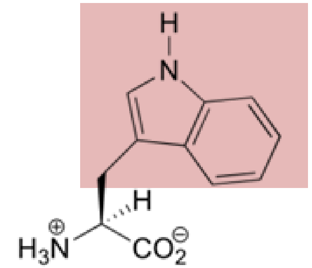
Aromatic side groups



Phenylalanine
Phe, F

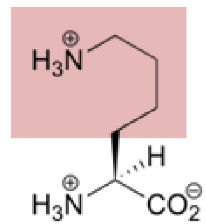


Tyrosine
Tyr, Y

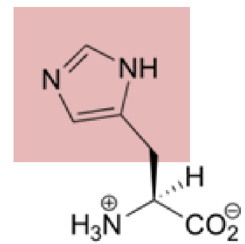


Tryptophan
Trp, W

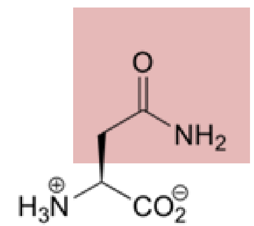
Positively charged side groups



Lysine
Lys, K

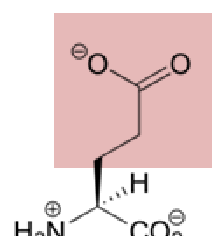


Histidine
His, H

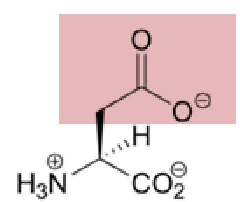


Asparagine
Asn, N

Negatively charged side groups



Glutamate
Glu, E

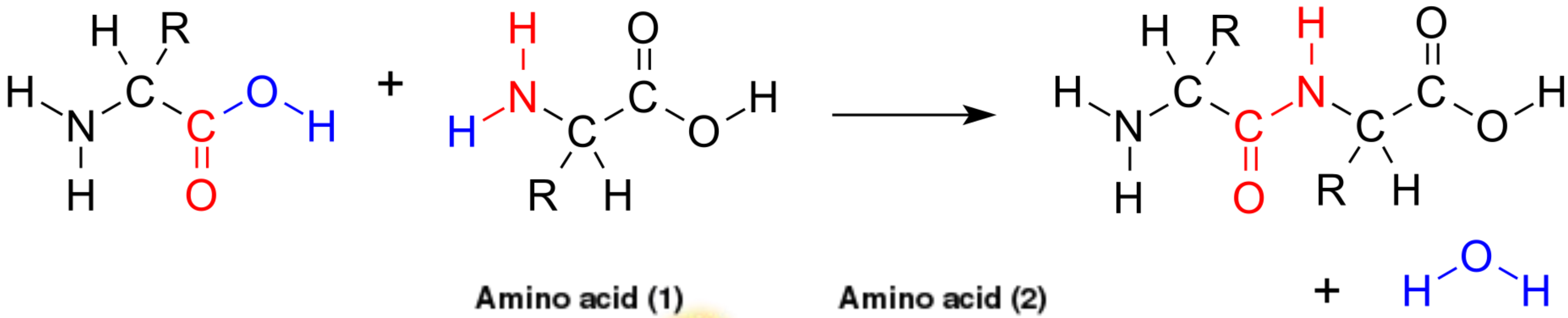


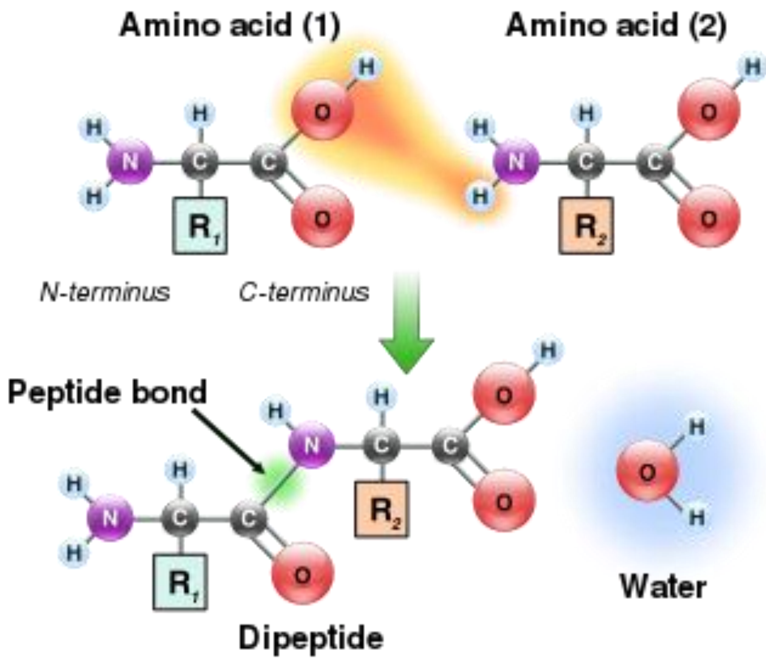
Aspartate
Asp, D

Protein structure

- Proteins show up to four levels of organisation:
  - Primary structure – the sequence of amino acids along the polypeptide backbone
  - Secondary structure – structural features arising through the peptide bond and intra or inter-strand hydrogen bonding. The alpha helix and the beta sheet are famous examples identified by Linus Pauling.
  - Tertiary structure – this corresponds to the folding of the protein governed by suparamolecular interactions such hydrogen bonding, hydrophobic interactions, salt formation between side chains of opposite charge, formation of disulfide bridges and templating effects of metal ions.
  - Quaternary structure – this is the assembly of protein subunits to give a superstructure.

Protein primary structure – the petide bond





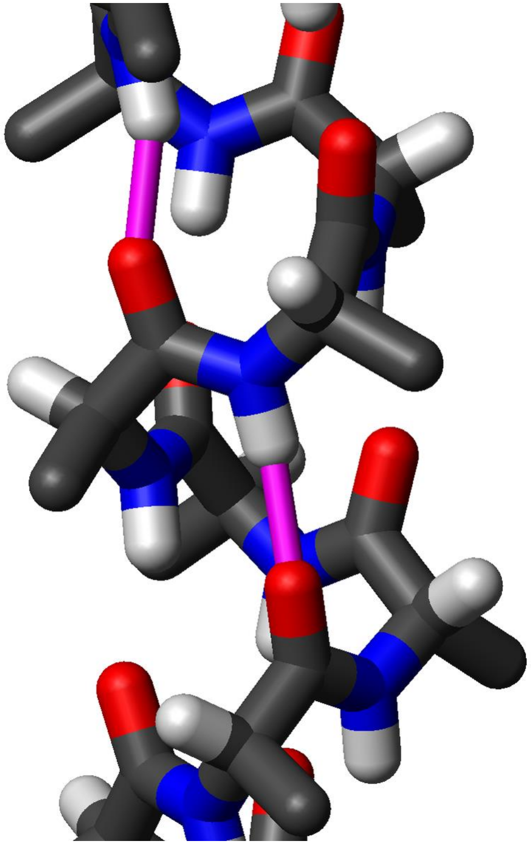
Properties of the peptide bond

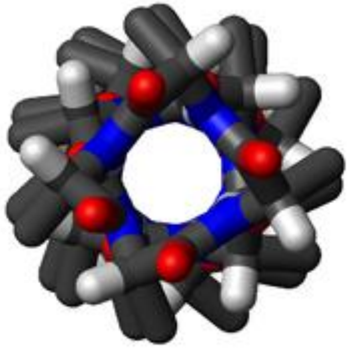
- The peptide bond is rigid and planar
- The atom sequence in a peptide bond is **C*α*-C-N-C*α*.**
- The peptide bond is coplanar, this indicated a **resonance** or partial sharing of two pairs of electrons between the carbonyl oxygen and the amide nitrogen.
- The 4 atoms of the peptide group (C, H, O, and N) lie in a single plane, in such a way that the oxygen atom of the carbonyl group and the hydrogen atom of the amide nitrogen are ***trans*** to each other.
- The peptide bond shows partial double bond character.
- This leads to the formation of characteristic secondary structural features involving hydrogen bonding between the NH of the peptide bond and C=O of another peptide bond unit.

α-helix and β-sheet secondary structures

The amino acids in an **α-helix** are arranged in a right-handed helical structure where each amino acid residue corresponds to a 100° turn in the helix - i.e., the helix has 3.6 residues per turn - and a translation of 1.5 Å (0.15 nm) along the helical axis.

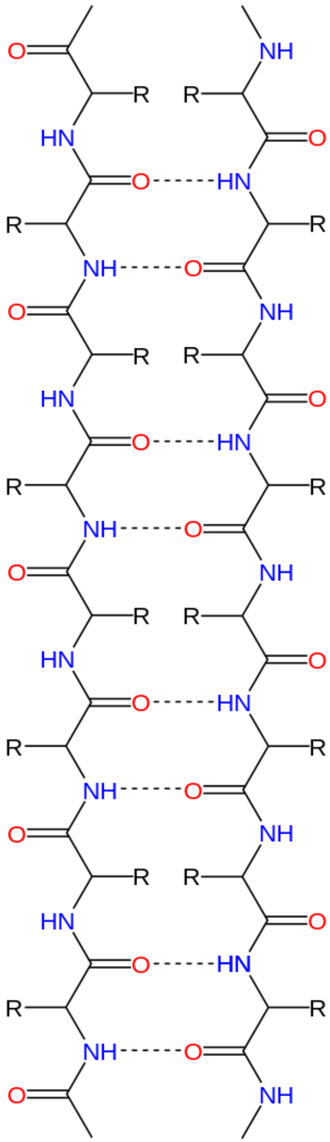
Side view of an α-helix of alanine residues.
Two hydrogen bonds for the same peptide group are highlighted in magenta.
The H to O distance is about 2 Å (0.20 nm).
The peptide chain runs upwards, i.e. its N-terminus is at the bottom and its C-terminus at the top.
The sidechains (black) are angled downwards towards the N-terminus
while the peptide oxygens (red) point up and the peptide NH groups down.





View down the helix.
Four carbonyl groups point upwards towards the viewer and spaced roughly 100° apart on the circle, corresponding to 3.6 amino acid residues per turn of the helix.

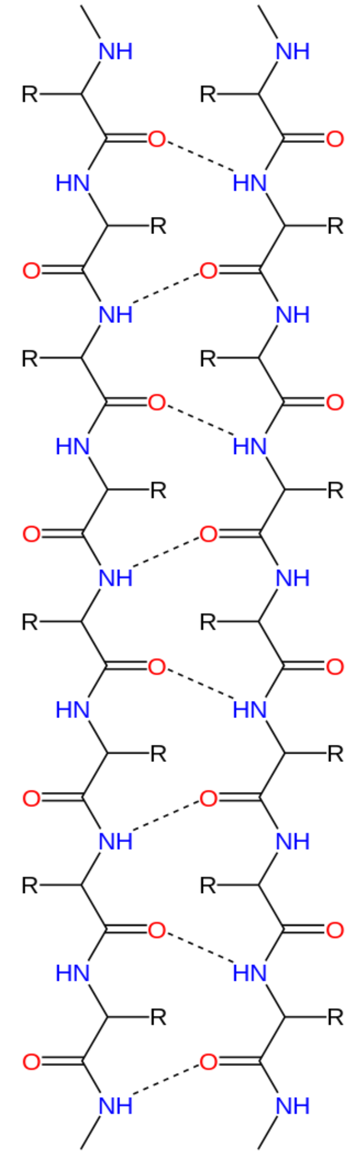
α-helix and β-sheet secondary structures



Whereas the H-bonding in the α-helix is intramolecular, in the β-sheet structure it is intermolecular and can be either with anitparallel strands (left) or parallel strands (right).

Small R groups are necessary for these structural arrangements and the structure can be induced by stretching the helices in wool so that the protein transforms from α-keratin to β-keratin.

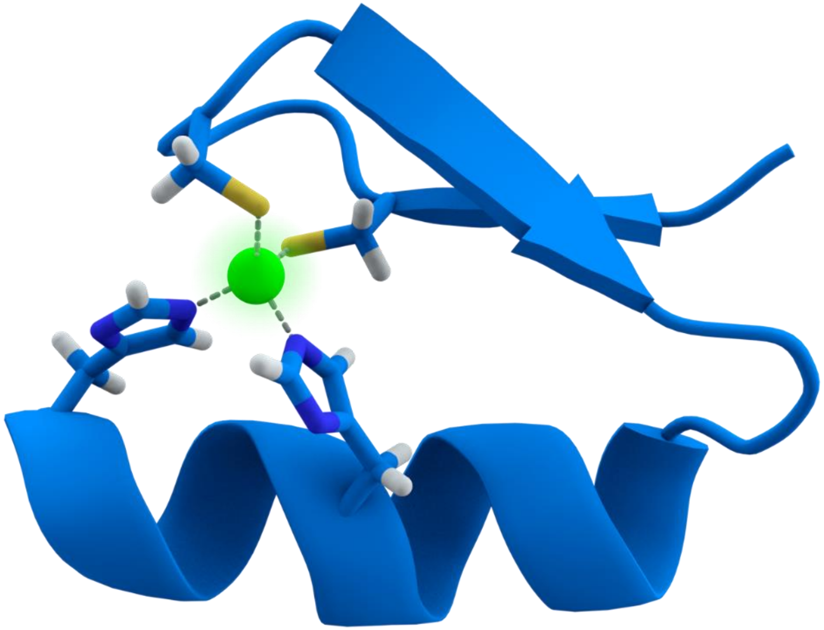
Silk also has this structure.



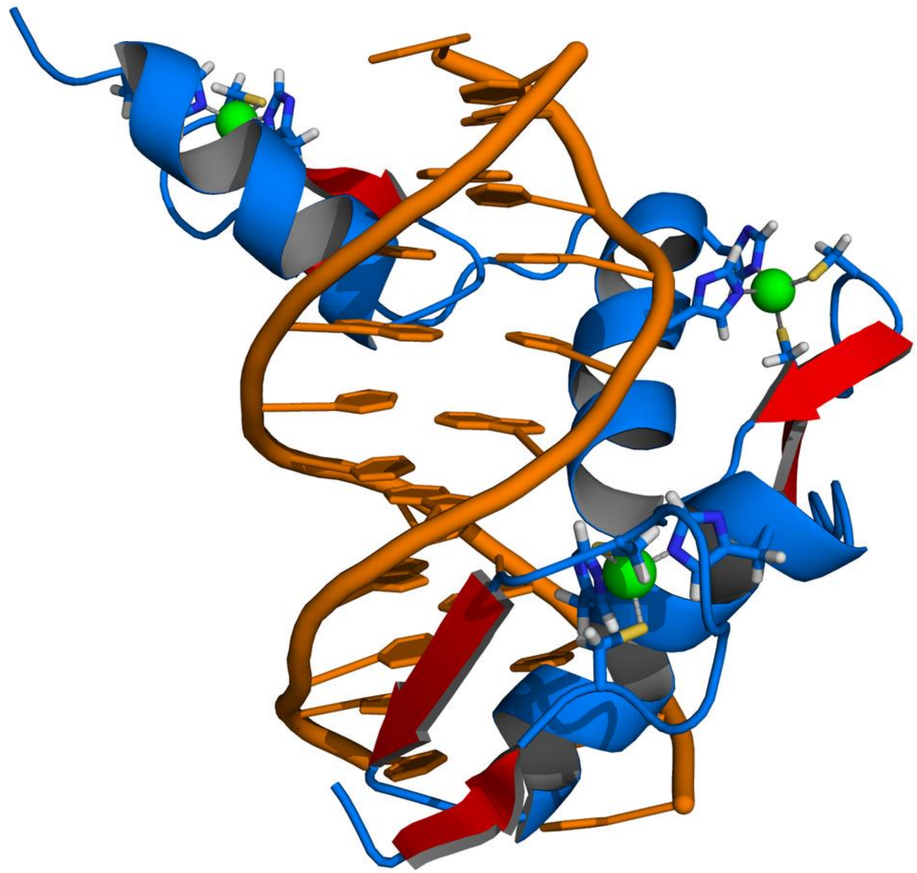
Tertiary protein structure

- The primary structure tells us the sequence of amino acids making up the protein backbone.
- The secondary structure is about how the peptide backbone is arranged in space.
- The tertiary structure is about how the sidechain groups on the α-amino acids can associate through supramolecular interactions mediated by hydrogen bonding, hydrophobic interactions or coordination to structural metal ions like Zn(II).

The Cys_2His_2 zinc finger motif consisting of an α helix and an antiparallel β-sheet. The green Zn(II) is coordinated by two histidine (N donors) and two cysteine (S donors).

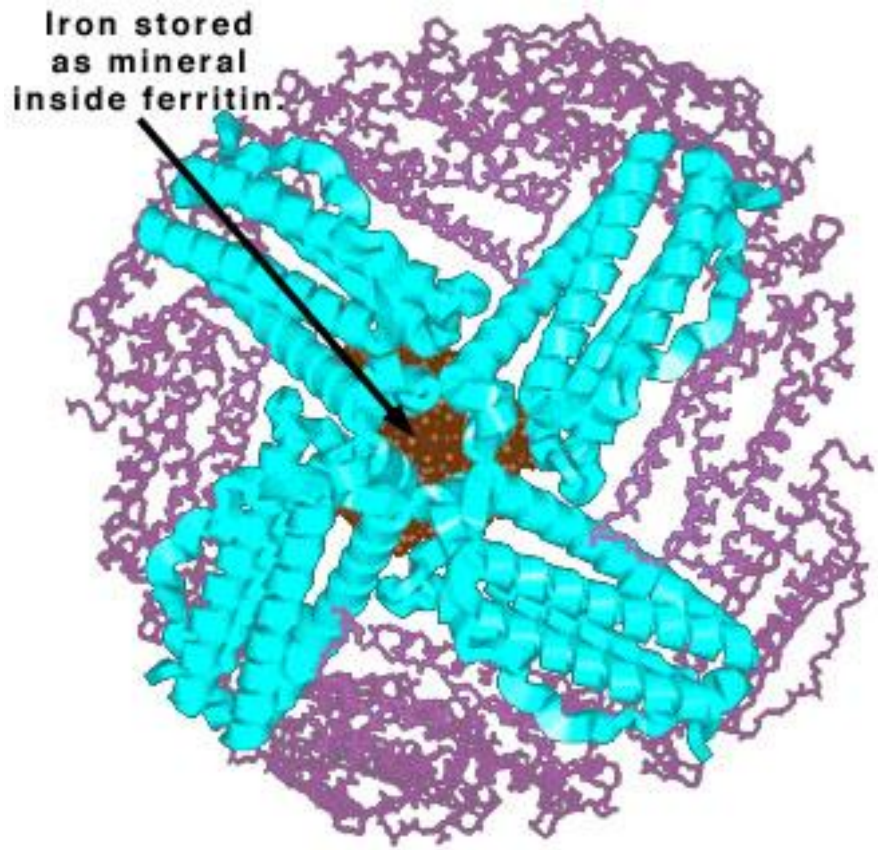


Cartoon showing how the protein Zif (Zinc Finger) 269 (blue) uses three fingers to interact with DNA (orange). The coordinating amino acid residues and (green) zinc ions are shown as atoms.



Quaternary structure

This is where identifiable protein units join together to produce larger entities – very common to have at least two subgroups as dimers and the iron storage protein ferritin has 24 subgroups which can be regarded as 12 dimers joined together to form a rhombic dodecahedron (polyhedron with twelve faces).

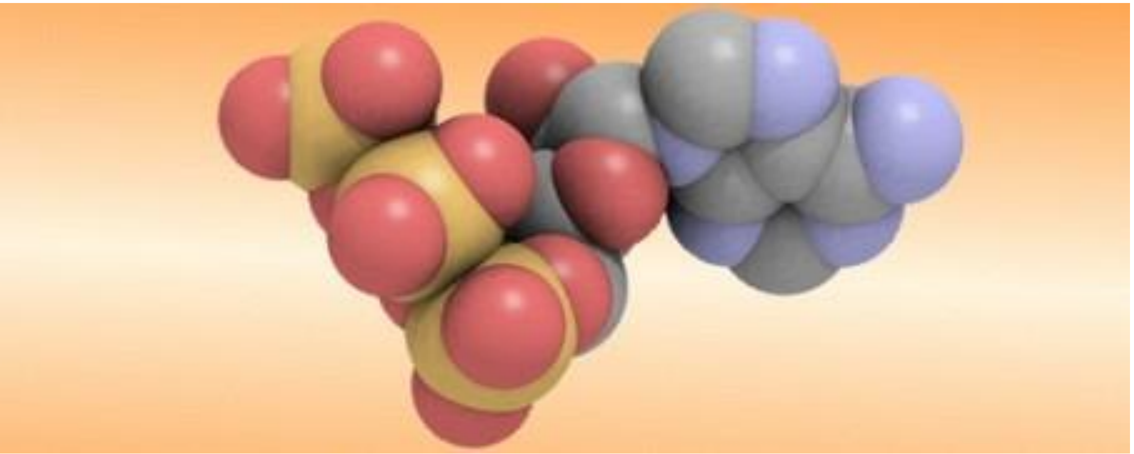


Biogeochemical Cycles 5

- In 1669 the German alchemist Henning Brand noticed that urine has a golden colour and wanted to discover whether he could isolate gold from it. He started collecting urine mostly from his wife and her friends – he probably collected around 7500 litres of urine over the course of his experiments.
- He first tried to boil some urine in a vat until it was a thick, syrup-like substance. This substance was glowing red-hot. After that, the substance hardened, cooled and turned black. He mixed the black part with the red and heated it. In the end, he distilled it and then it burst into flames.
- He thought he had discovered the Philosopher's Stone. He didn't know that he had discovered phosphorus, one of the most important elements of all.
- Brand named the new discovery phosphorus, from the Greek for "light bearer." He didn't tell anyone about his discovery for six years because he thought that people would steal it from him.
- He made even more experiments but after six years he realized that he didn't discover the philosopher's stone, but something else that was unknown to him.
- He was the first person to discover a new element i.e. not simply identify something that was known, like oxygen, but discover a hitherto unknown element.

The Alchemist in Search of the Philosophers Stone (1771) by Joseph Wright depicting Hennig Brand discovering phosphorus.

Some important biomolecules - ATP



Phosphorus is relatively rare on Earth, but is essential for life. The element P shows up in a surprisingly wide range of biological molecules. For instance, one of the best known molecules for carrying energy around our bodies is adenosine triphosphate (ATP).

Until recently, the leakage of phosphorus at all stages of the food production cycle was occurring with little fanfare, and phosphorus was more often than not labelled a pollutant for its effects on our waterways. Within the past five years, however, Australian-led research has sparked an international effort to raise awareness and foster sustainable management of this non-renewable resource which forms the basis of the global fertiliser industry.

Investigations by Dr Dana Cordell and Professor Stuart White from the Institute for Sustainable Futures at the University of Technology, Sydney predict that without action and at current rates the world will have consumed its best supplies of phosphorus within 20 years and may exhaust them by 2050.

http://eureka.australianmuseum.net.au/eureka-prize/environmental-research5

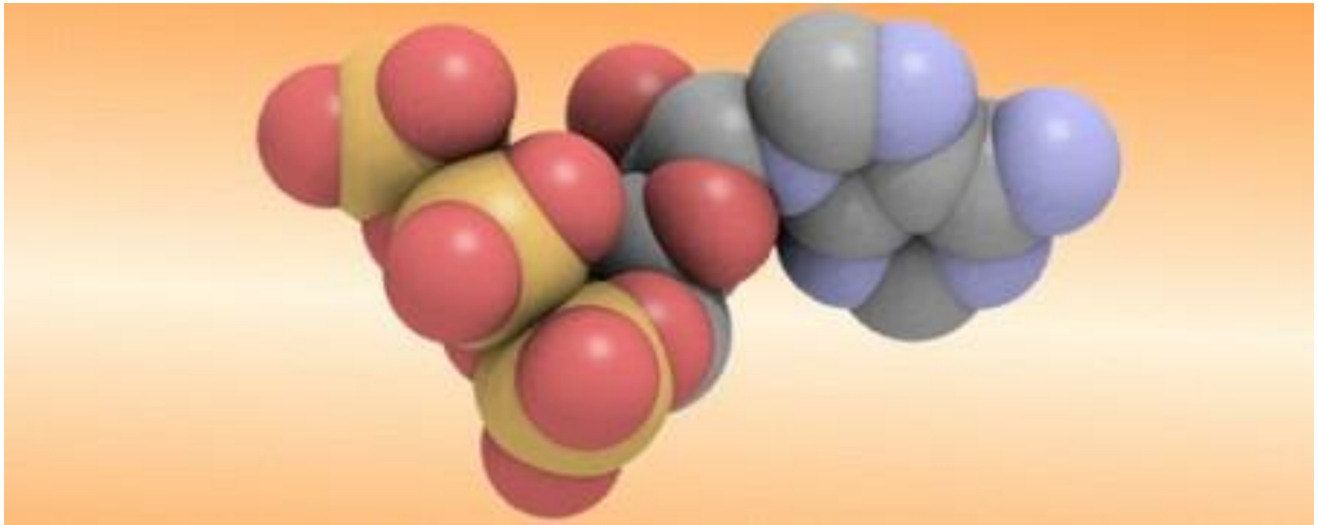
Environmental Research – Conserving life's building block

For their breakthrough work identifying phosphorus scarcity, tracking its life cycle and developing global and regional scenarios for its sustainable production and consumption, Dr Cordell and Professor White have been awarded the 2012 NSW Office of Environment and Heritage Eureka Prize for Environmental Research.

The Hon Robyn Parker MP, Professor Stuart White and Dr Dana Cordell
Photographer: Daniel O'Doherty

Some important biomolecules - ATP

- Metabolic processes that use ATP as an energy source convert it back into its precursors. ATP is therefore continuously recycled in organisms: the human body, which on average contains only 250 grams (8.8 oz) of ATP,[turns over its own body weight equivalent in ATP each day.

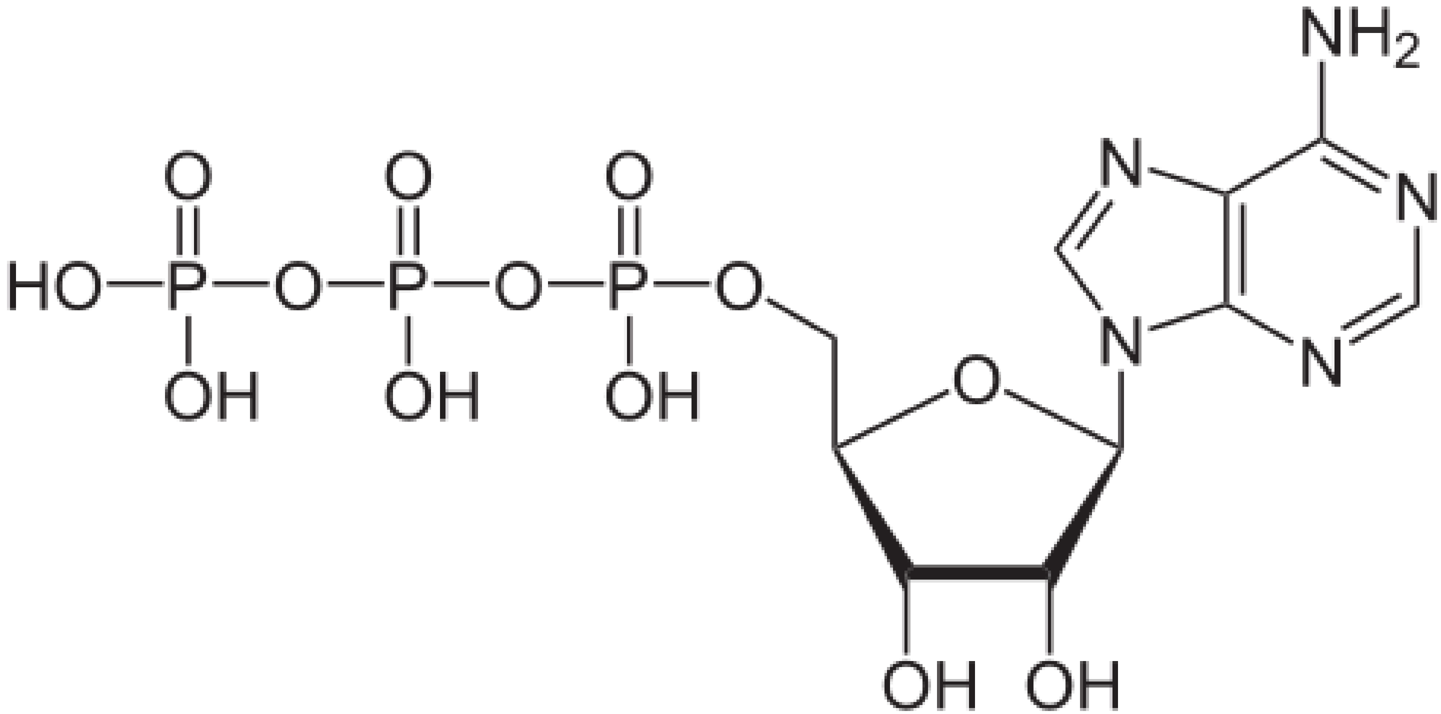


David E. Bryant, Katie E. R. Marriott, Stuart A. Macgregor, Colin Kilner, Matthew A. Pasek, Terence P. Kee. **On the prebiotic potential of reduced oxidation state phosphorus: the H-phosphinate-pyruvate system**. *Chemical Communications*, 2010; 46 (21): 3726 DOI: 10.1039/c002689a

Some important biomolecules - ATP

- All living things, plants and animals, require a continual supply of energy in order to function. The energy is used for all the processes which keep the organism alive.
- Some of these processes occur continually, such as the metabolism of foods, the synthesis of large, biologically important molecules, *e.g*. proteins and DNA, and the transport of molecules and ions throughout the organism.
- Other processes occur only at certain times, e.g. muscle contraction.
- Animals obtain their energy by oxidation of foods and plants by trapping sunlight using chlorophyll.
- Before the energy can be used it must be transformed into a form which the organism can handle easily. **This special carrier of energy is the molecule adenosine triphosphate, or ATP.**
- The ATP molecule is composed of three components.
- At the centre is a sugar molecule, ribose (same sugar as found in DNA).
- Attached to one side of this is the purine base adenine (also found in DNA).
- The other side of the sugar is attached to a string of phosphate groups.
- The phosphates are the key to the activity of ATP.

Chemical structure of ATP



ATP consists of a base – far right - in this case adenine;
a ribose – middle
and a phosphate chain - left

How ATP works

ATP works by losing the endmost phosphate group when instructed to do so by an enzyme.

This reaction releases a lot of energy, which the organism can then use to build proteins, contract muscles, *etc*.

The reaction product is adenosine diphosphate (ADP), and the phosphate group either ends up as orthophosphate (HPO_4) or attached to another molecule (*e.g*. an alcohol).

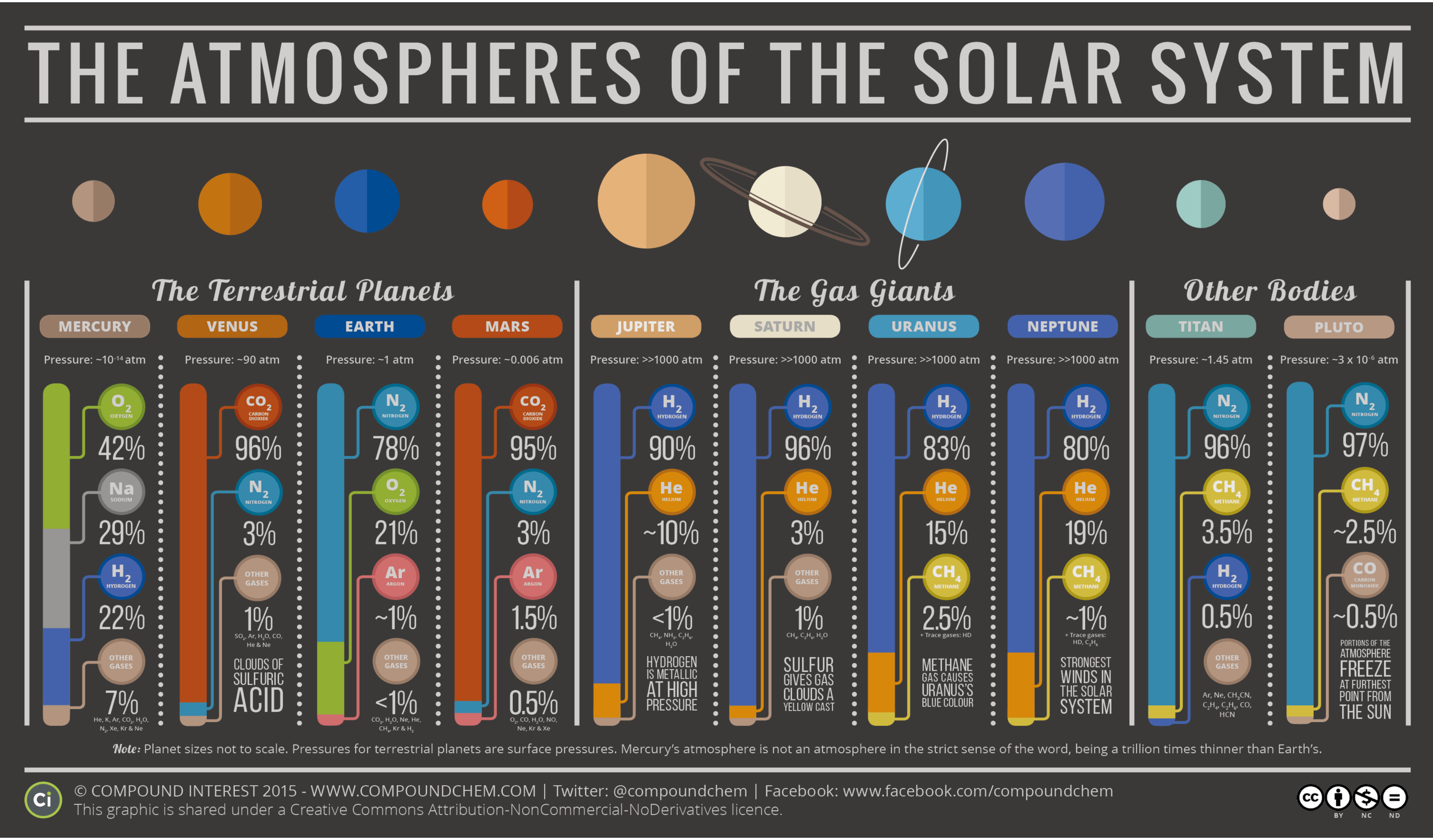
$$ATP + H_2O \longrightarrow ADP + HPO_4$$

Even more energy can be extracted by removing a second phosphate group to produce adenosine monophosphate (AMP).

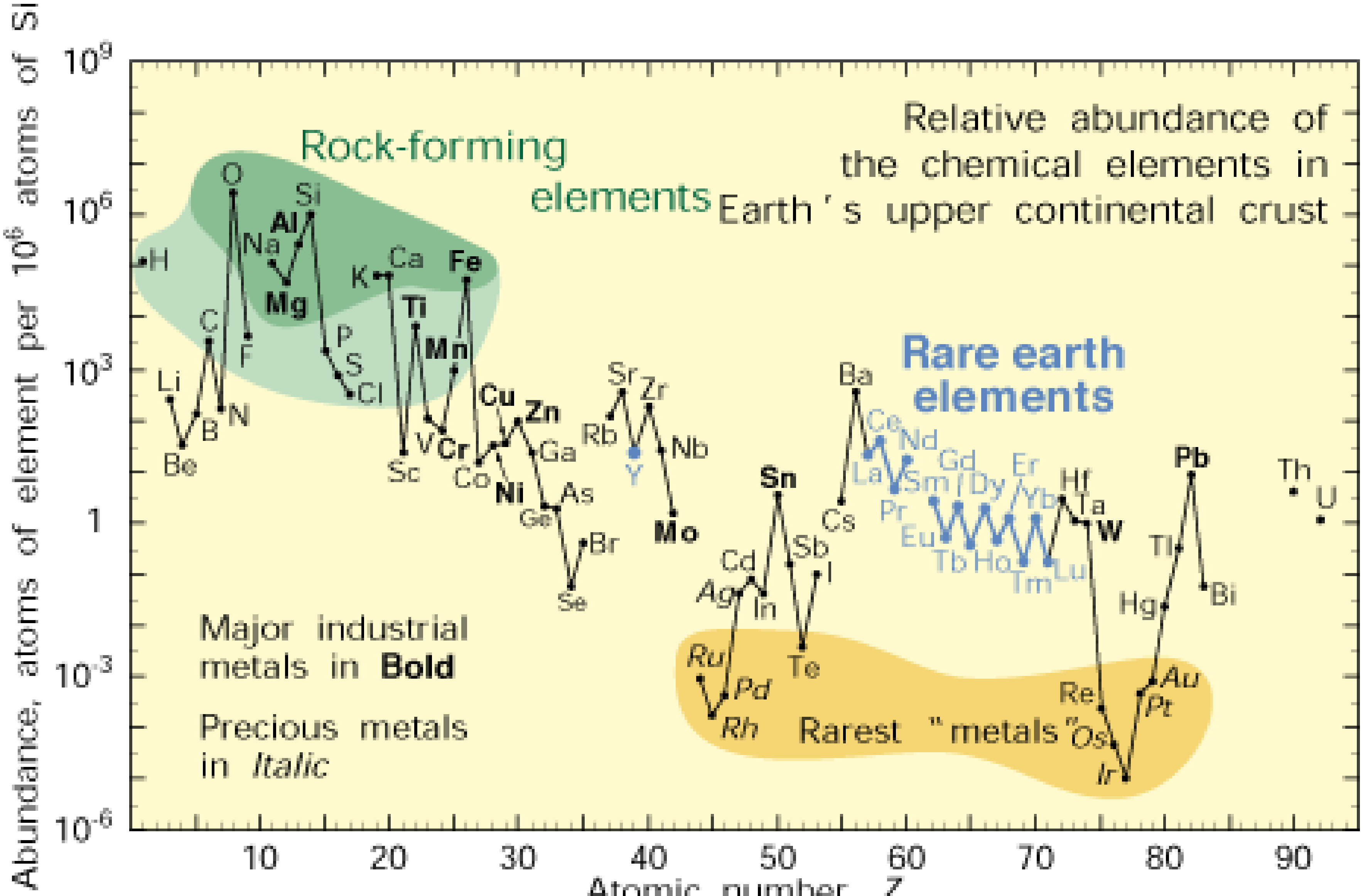
When the organism is resting and energy is not immediately needed, the reverse reaction takes place and the phosphate group is reattached to the molecule using energy obtained from food or sunlight.

Thus the ATP molecule acts as a chemical 'battery', storing energy when it is not needed, but able to release it instantly when the organism requires it.

Compositions of atmospheres of planets

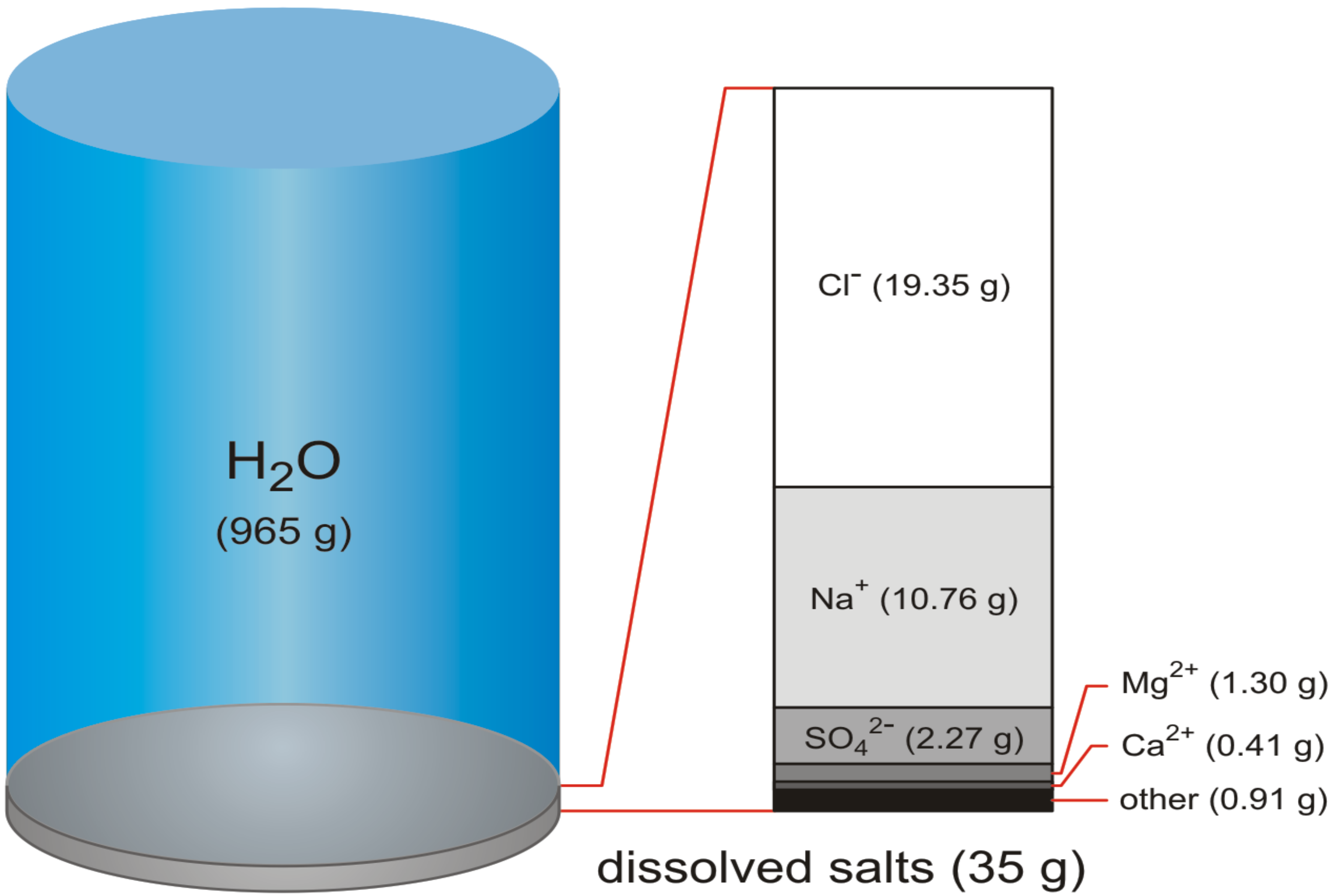


Relative abundance of elements in upper crust of Earth

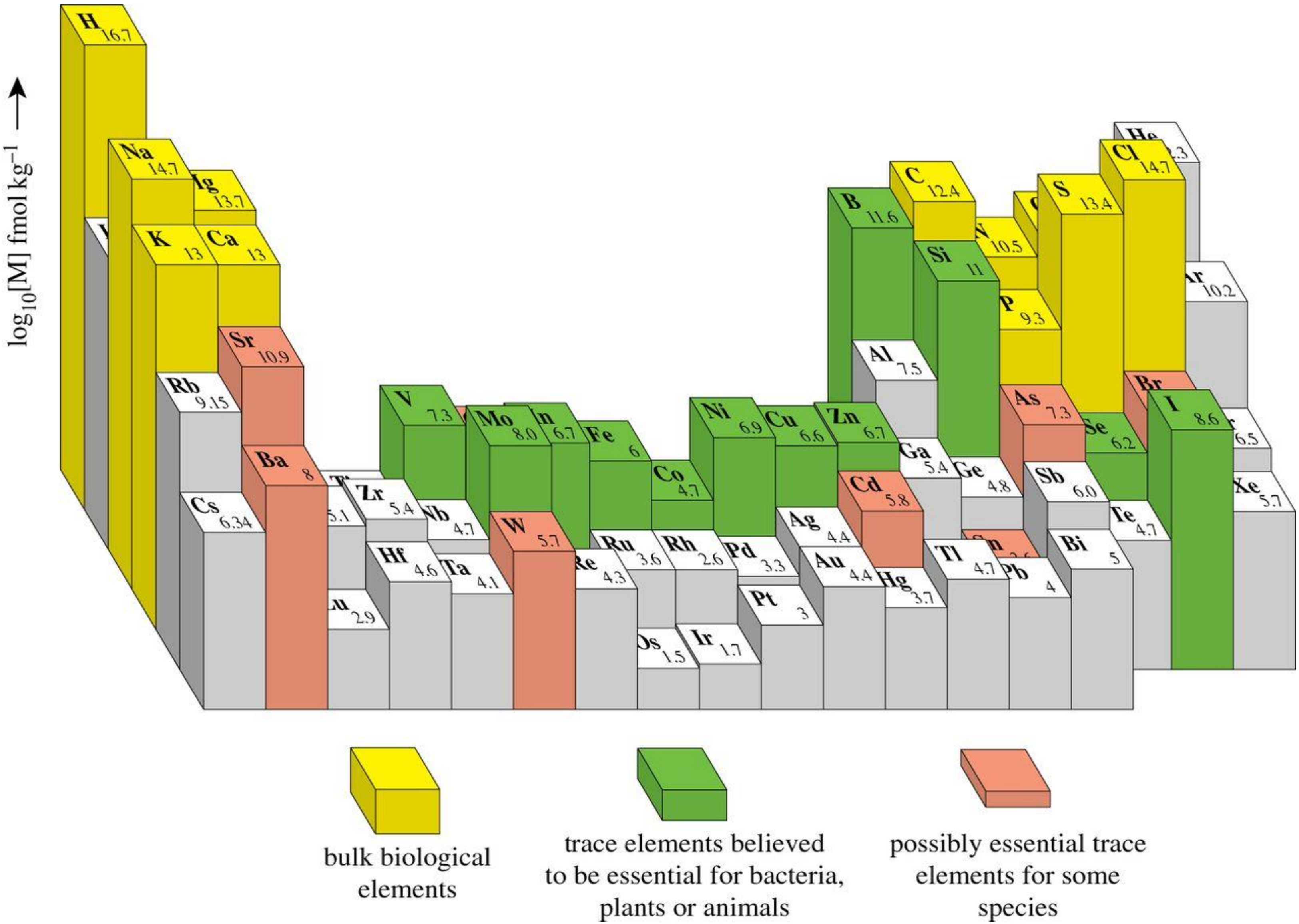


Composition of seawater

Chemical composition of 1 kg seawater with a salinity of 35 ‰



Biologically important elements



Element	Universe	Earth's Crust	Earth's Ocean	Earth's Air	Human body
Oxygen (O)	1.07	46.71%	85.84%	20.9%	65.0%
Silicon (Si)	0.065	27.69			
Aluminium (Al)		8.07			
Iron (Fe)	0.109	5.05			
Calcium (Ca)		3.65	0.04		1.5
Sodium (Na)		2.75			0.2
Potassium (K)		2.58	0.04		0.4
Magnesium (Mg)	0.058	2.08	0.1292		0.1
Titanium (Ti)		0.62			
Hydrogen (H)	73.9	0.14	10.82	variable	9.5
Phosphorus (P)		0.13		trace	1.0
Carbon (C)	0.46	0.094	0.0028	variable	18.5
Manganese (Mn)		0.09			
Sulphur (S)	0.044	0.052	0.091	trace	0.3
Barium (Ba)		0.05			
Chlorine (Cl)		0.045	1.94		0.2
Chromium (Cr)		0.035			
Fluorine (F)		0.029			
Zirconium (Zr)		0.025			
Nickel (20)		0.019			
Bromine (Br)		trace	0.0067		
Nitrogen (N)	0.095	trace		78.1	3.3
Argon (Ar)		-	-	0.96	-
Helium (He)	24.0	-	-		-

Comparative Chart of Element abundance

The Universe is ca 13.8 billion years old and composed of: 73% dark energy, 23% dark matter and only 4% atoms (chemical elements).

The mystery around phosphorus

- Phosphorus is much more abundant in lifeforms than expected and seems to play very important roles in biochemistry.
- For example, it is used in ATP, is a major constituent of bones and teeth in many mammalian skeletons, is part of both RNA and DNA, is part of the lipids which form cell membranes and is yet astronomically not expected to be as abundant on Earth as it actually is.
- Looking at the many roles that P play in biology, it is hard to imagine how life could do without it.
- Investigations into how phosphorus species took a decisive role in the evolution of life on Earth have revealed some interesting facts.

Importance of phosphate in DNA and RNA

- An important role is played by phosphates, for example both DNA and RNA have a sugar-phosphate backbone. The phosphate PO_4^{3-}, works as a kind of "super glue," since it has three oxygen atoms that will carry charges in solution.
- Two of these oxygen atoms form ionic bonds with two neighboring sugars, while the third oxygen is left "dangling" with a negative charge that makes the whole DNA or RNA molecule negatively charged.
- This overall charge helps to keep the molecule from drifting out of its proscribed location.

Where did P come from and where does it go?

- The most common elements in a typical cell are hydrogen, oxygen, carbon, nitrogen, phosphorus and sulfur. Apart from P these are all in the top ten of the elements in the solar system – P is in 17th place.
- This scarcity of phosphorus is even more acute on the Earth's surface, where much of the phosphorus is locked up in phosphate minerals that life has difficulty making use of.
- How did life come to utilise this relatively scarce element?
- When and how phosphorus entered into life is not known.
- It is possible that early life did not use P at all or only in traces.
- In nucleic acid systems the "glue" role of phosphate could have been filled by glyoxylate, a molecule still used in organisms.
- But the use of phosphate seems to have brought life to a higher level.

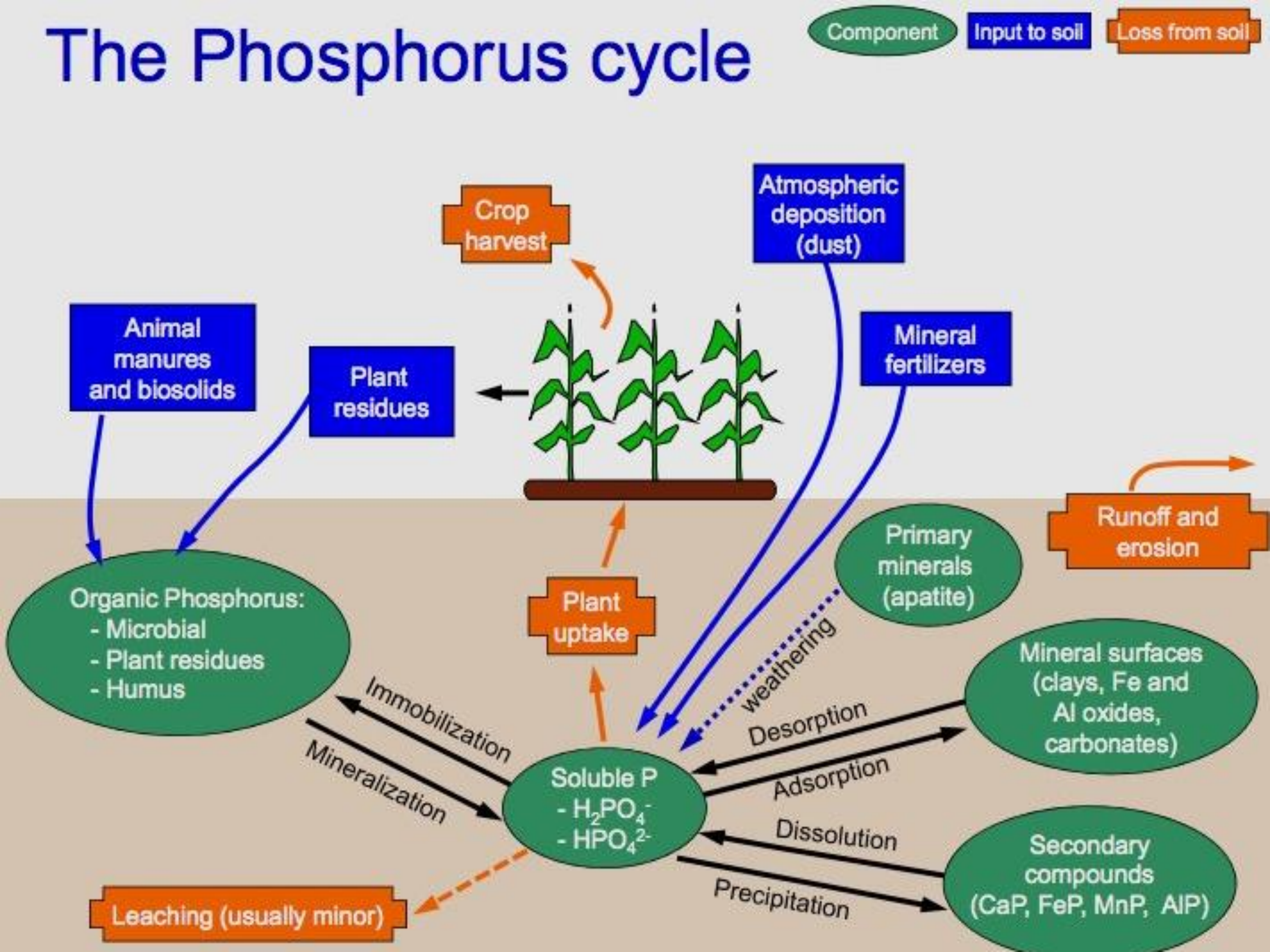
Where did P come from and where does it go?

- Once biology had realised the potential of using phosphate-based biomolecules, there was a need to ensure its supply.
- Humans and other animals get their phosphorus from eating plants (or by eating animals that eat plants).
- Plants aren't able to recycle all of the available phosphorus in the soil, so some of it ends up going into the ocean.
- There, it can be used by marine organisms, but eventually the phosphate settles on the seafloor where it becomes incorporated into rock sediments.
- Once the phosphorus is locked up in insoluble minerals, it takes a very long time for it to return to a form that plants and other organisms can use.

The Phosphorus Cycle

- The phosphorus cycle is one of the slowest element cycles of biological importance.
- Being too impatient to wait for geological processes to free up phosphorus, humans simply mine "rock phosphate" and chemically modify it to make fertiliser for growing more plants.
- So, given the slowness of the natural P cycle, and the fact that most of the phosphorus on the Earth's surface is found in some type of phosphate, which is the thermodynamically most stable for of P in the oxygen-rich environment, how did biology grab P for itself?
- It seems that the more reduced form of phosphides would be suitably bioavailable, but these minerals are found 3000 km below the surface of the Earth.
- This seems puzzling…

The Phosphorus cycle



P from heaven

- The answer seems to lie in the stars!
- Although most of Earth's phosphide is found in the core, on the surface, one of the most common, naturally-occurring phosphides is schreibersite, which originates not from below the surface of the Earth, but has been rained in from above in the form of meteorites.
- Meteorites originate from rocky debris forming the "Asteroid belt" between Mars and Jupiter and earlier in the Earth's history meteorites would have bombarded the surface of the Earth.
- The results of such bombardments are still clearly visible on the surface of the Moon and of Mars.
- Luckily, these events are now fairly rare, but can be spectacular, like the recent meteorite hit in Russia.

The possible incorporation of P into life on Earth

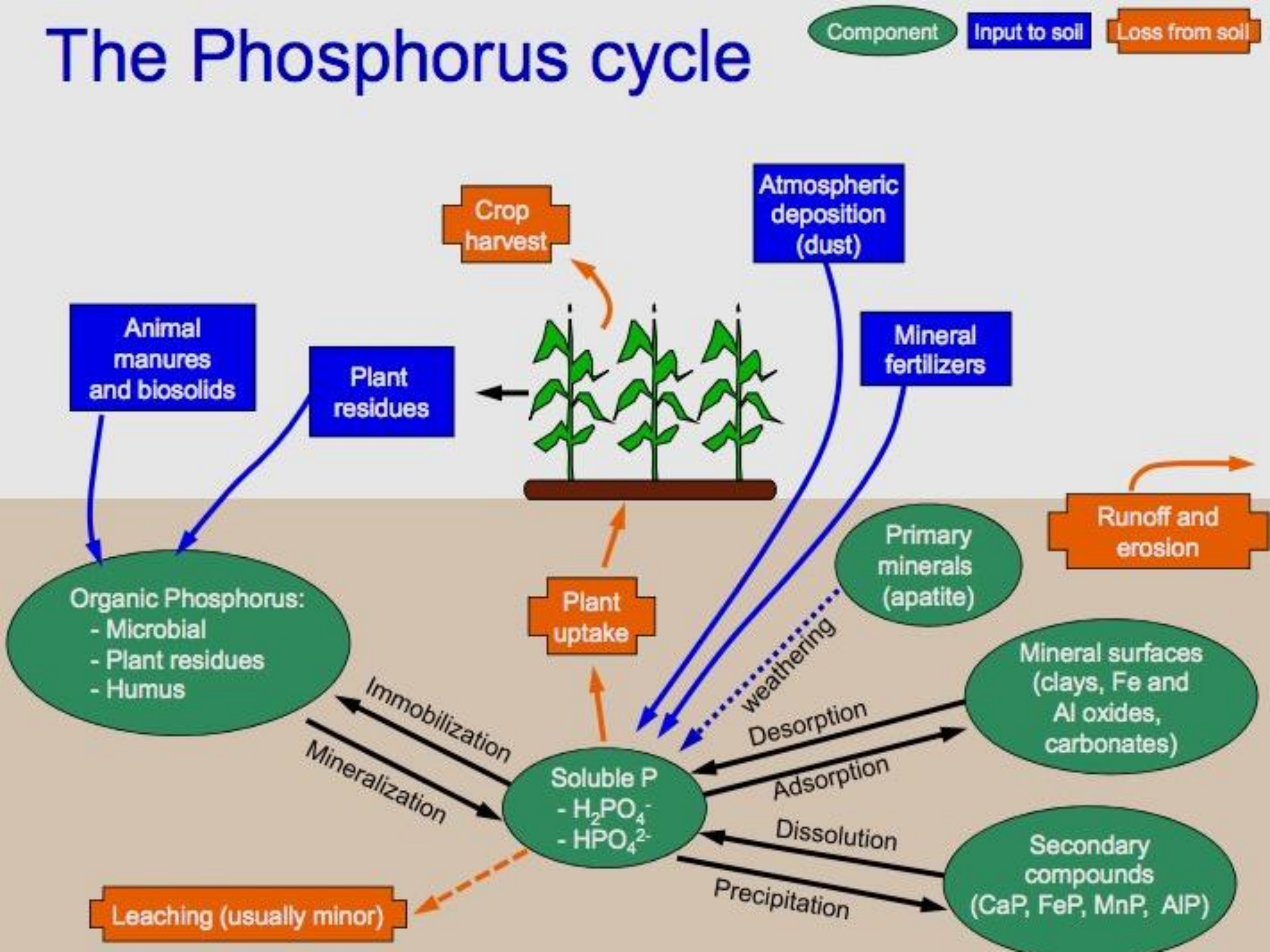
- A current theory by Matthew Pasek developed during his PhD studies (Univ. Arizon, 2006) suggests that biological use of phosphides as a source for phosphates allowed life to develop over the first 2 billion years of the Earth's history.
- This is supported by computer modelling studies.
- These also indicate that that most of the phosphides on the Earth's surface came from meteorites.
- Furthermore, triphosphate materials as found in ATP can isolated from "promordial soups" containing phosphides and organic compounds.
- Matthew Pessac is now Assoc. Prof. at the Univ. of South Florida: http://hennarot.forest.usf.edu/main/depts/geosci/faculty/mpasek/

Is man's use of P a problem?

- Over time, much of this meteoric phosphide has transformed to phosphates and it is estimated that 1 to 10 % of phosphates found on Earth today came from meteorites.
- Clearly, the fact that cycling P is a lengthy process and we are not doing much to recycle what we use, dispersing it in the oceans instead, poses some problems…
- There is currently a project at MIT called Mission 2016, which addresses the problems of element recycling and provides possible solutions. web.mit.edu/12.000/www/m2016/finalwebsite/
- These range from "becoming environmentally responsible" to "raiding the next available environments" – e.g. asteroid mining…

web.mit.edu/12.000/www/m2016/finalwebsite/solutions/phosphorus.html
web.mit.edu/12.000/www/m2016/finalwebsite/solutions/asteroids.html

The Phosphorus cycle



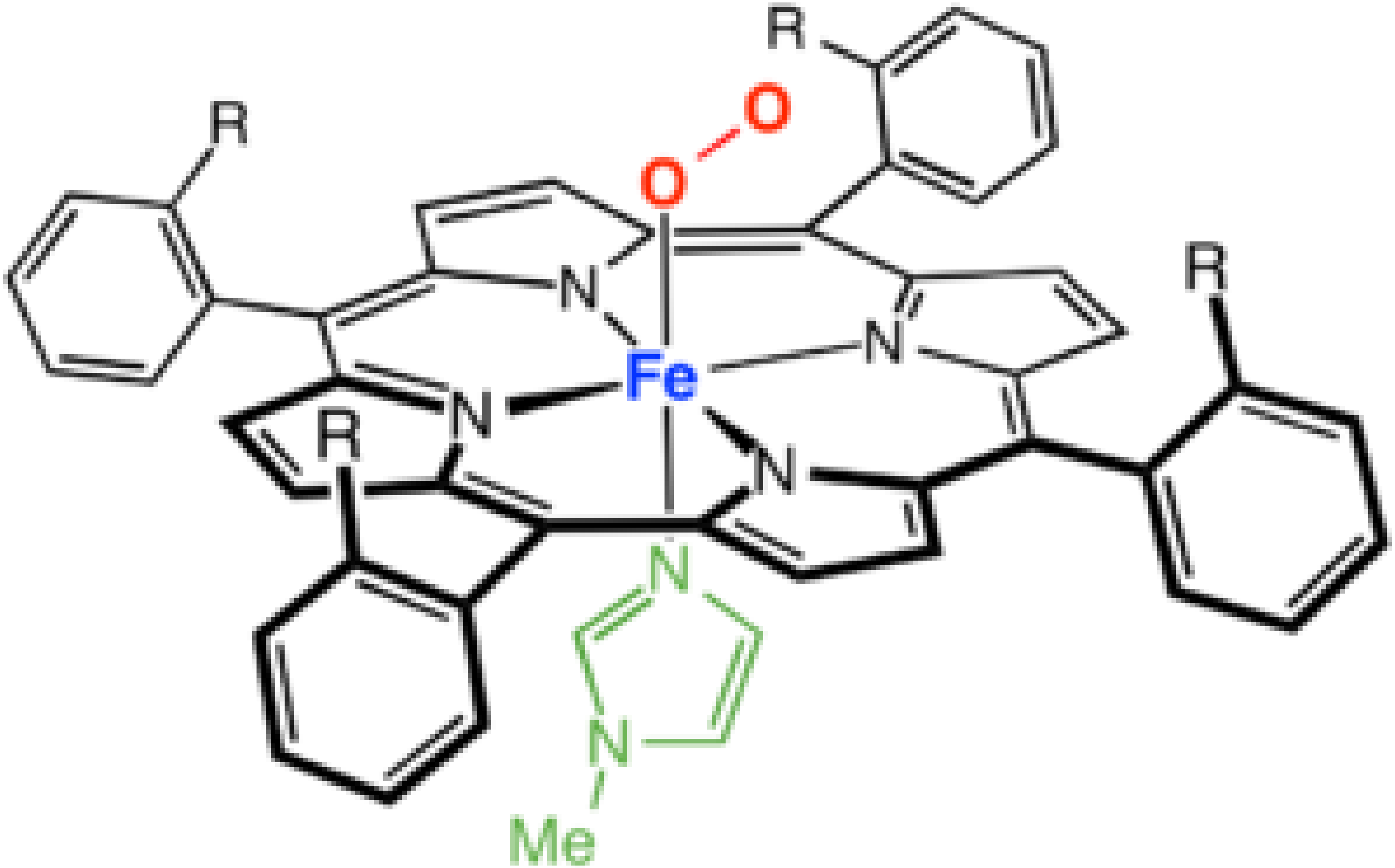
Biogeochemical Cycles 6: Bioavailability

- Bioavailability describes whether a chemical element - native or as part of a molecule or ion – can be utilised by biology.
- We already noted that bioavailabilty can change if changes are made to the environment.
- Comparing biological evolution with the levels of bioavailabilty of many metal ions can explain why some are favoured over others, but the natural abundance can also be important.
- The two commonest “trace elements” in biology are iron and zinc.
- Whilst iron has become dramatically less bioavailable due to the creation of an oxidising atmosphere leading to insoluble oxyhydroxides and oxides…
- The only thing that has changed for zinc is the reduction in sulfide species (which used to render zinc insoluble) and so zinc is now more bioavailable.

Iron metalloproteins

- Iron is the most abundant transition metal in the biosphere and apparently exists in all life forms.
- The range of functions iron metalloproteins show is huge thanks, in part, to the wide range of oxidation and spin states available.
- Since the Earth's atmosphere became oxidising, biology has developed a number of new enzyme systems to deal with problem of free Fe(III) ions producing free radical species (see Fenton reactions).
- Some are also based on iron, such as some catalases, others on Mn as well as Cu/Zn or Fe/Cu SOD systems.
- Iron sulfur proteins are useful for electron storage as well as forming part of the structure of the cofactor (FeMoCo) responsible for N_2 fixation in nitrogenase.
- Alongside haem and iron-sulfur proteins there are the Fe transport and storage proteins transferrin and ferritin.
- Ferritin offers a safe storage site for Fe which is hard for most systems to take-up and therefore largely gets recycled (you take-up less than 10 % of your daily iron intake!)

Haem proteins



Haem proteins

- Haem proteins contain Fe in various oxidation states trapped within a derivative of the macrocycle porphyrin.
- Myoglobin (oxygen storage) and haemoglobin (oxygen transport) are famous examples and were the first proteins to be structurally characterised using X-ray crystallography.
- John Kendrew and Max Perutz received the Nobel prize in 1962 in honour of this achievement. See: http://dx.doi.org/10.1016/j.jmb.2009.05.087 for the background story
- Even today, solving a protein crystal structure is very demanding, a major challenge being to obtain crystals of the protein at all.
- It should be remembered that the resulting structure is nearly always of the protein in its “resting state”. So mechanistic details need to be worked out using other techniques.

Multicellualar life using and dealing with oxygen

- Inhaled oxygen is delivered to red blood cells to transport it to every cell in the body.
- The advent of aerobic respiration added the oxygen-utilising tricarboxylic acid aka Krebs aka citrate) cycle and electron transport system to the anaerobic glycolysis - break down of glucose – system of anaerobes.
- This made it possible for aerobic organisms to extract 18 times more energy from glucose in the form of ATP via the Krebs cycle.
- Initially, organisms relied on diffusion to transport oxygen to their cells, but this is an inefficient, so they remained microscopic in size.
- The development of an obvious body required a circulatory system, initially very primitive and still small.
- E.g., nematode worms have a primitive type of body cavity (pseudocoelom) and circulation, consist of just under a 1000 cells and are only just visible with the naked eye.
- The development of a truly circulatory system to transport the highly specialised red blood cells to deliver oxygen to every cell in the body, no matter how large the organism, meant that body size was able to expand radically.
- At present the largest animal on Earth is the blue whale, weighing up to 150 tonnes and stretching over 30 metres in length from head to tail.

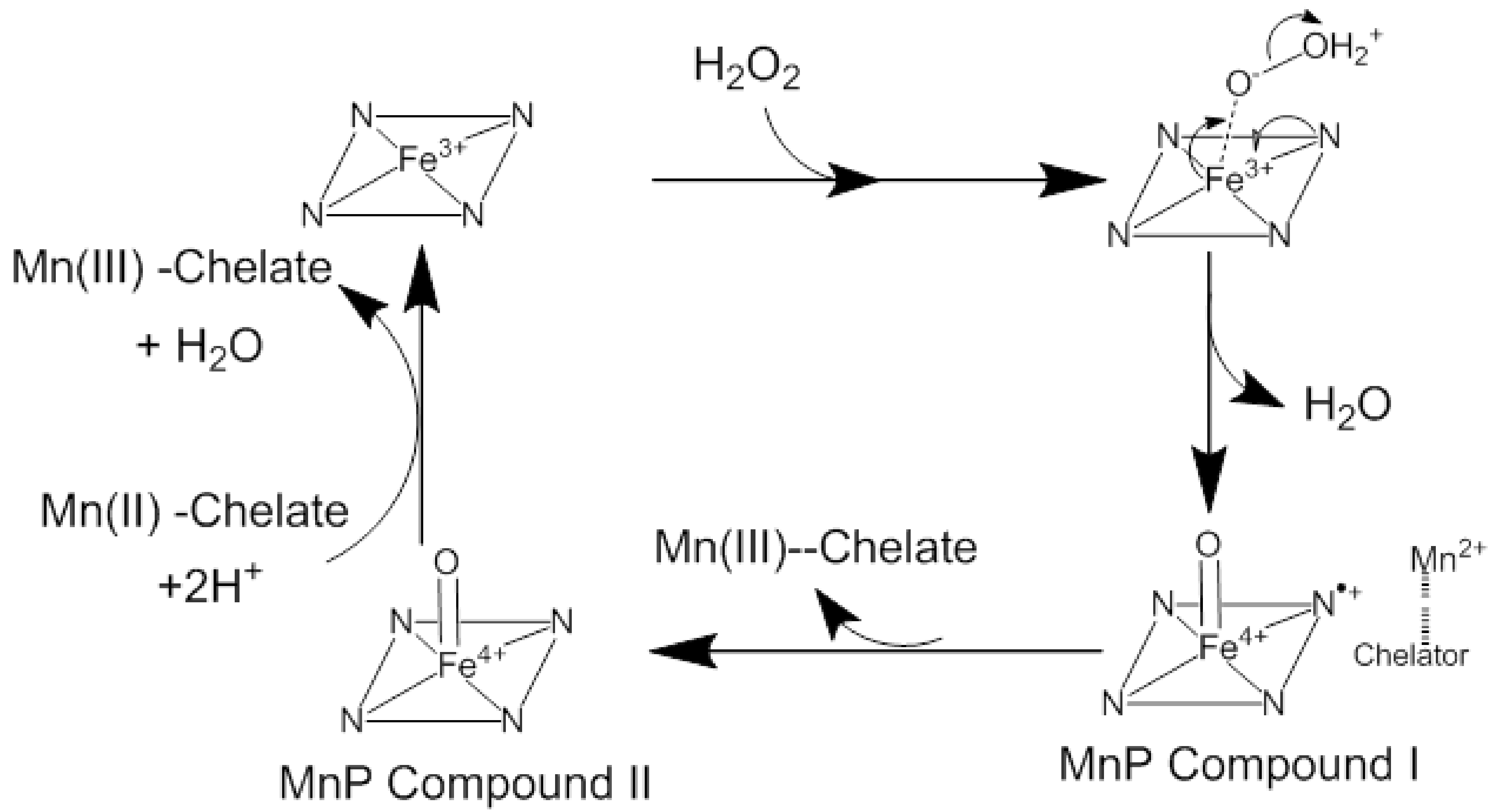
The blue whale makes the giant lizard – dinosaur diplodocus – look quite small

Haem proteins

- In myoglobin and haemoglobin the iron is in the Fe(II) state and actually cycles between high spin (deoxy form) and low spin (oxy form) states. The coordination number is always 6.
- In other haem proteins the iron can be in oxidation states as high as +5 and coordination numbers can vary from 4 to 6.
- Change of oxidation state of the iron allows for a broad span of electrical potential to be covered, important for redox processes designed to mop up the consequences of the presence of oxygen in biological systems.
- Examples include dealing with peroxides (O_2^{2-}) and superoxides (O_2^{-}).
- Manganese peroxidase utilises Mn(II), protons and hydrogen peroxide as substrates and relies on a haem cofactor to cycle electrons and bind the peroxide.

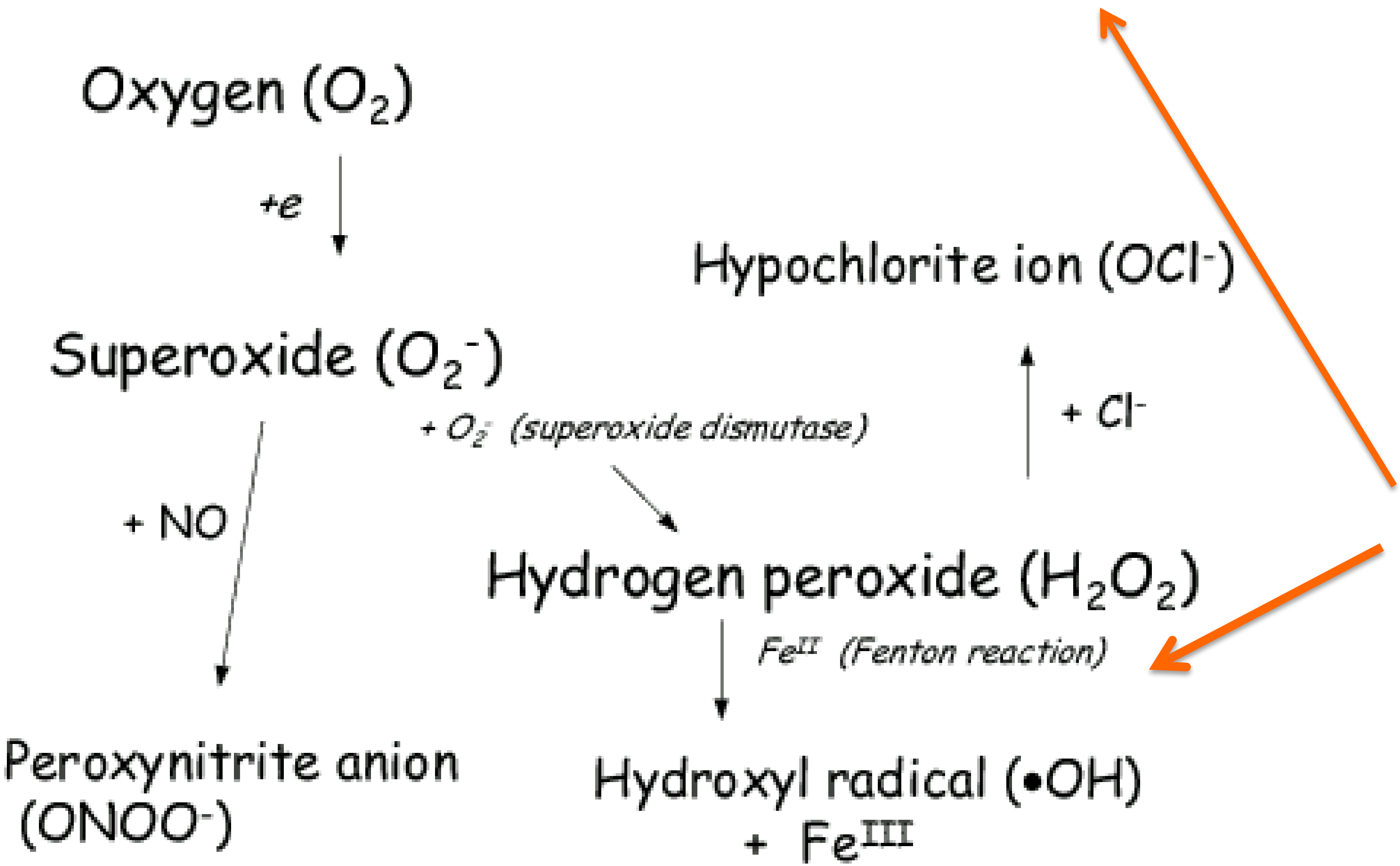
Manganese peroxidase

$$2Mn^{II} + 2H^{+} + H_2O_2 \longrightarrow 2Mn^{III} + H_2O$$

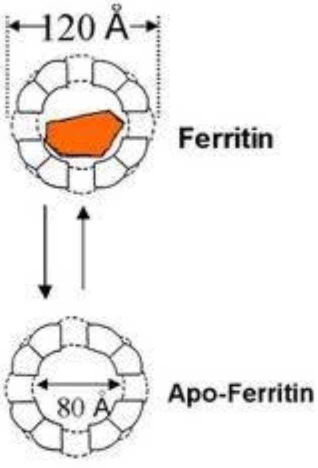


Why these oxygen species need to be dealt with: hydroxyl radicals must be avoided.

Fenton reaction: $Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + OH^{\cdot} + OH^-$

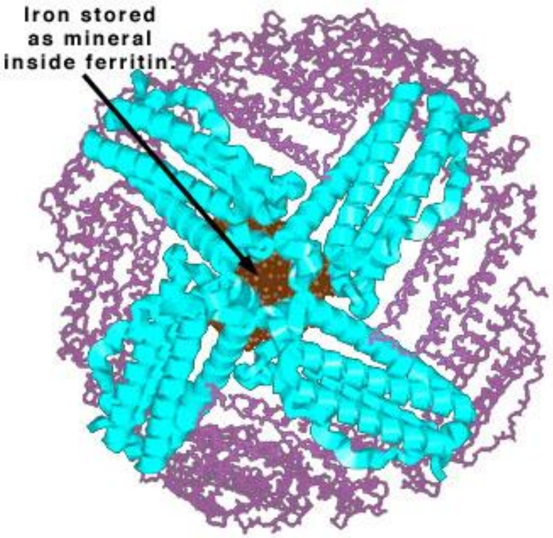


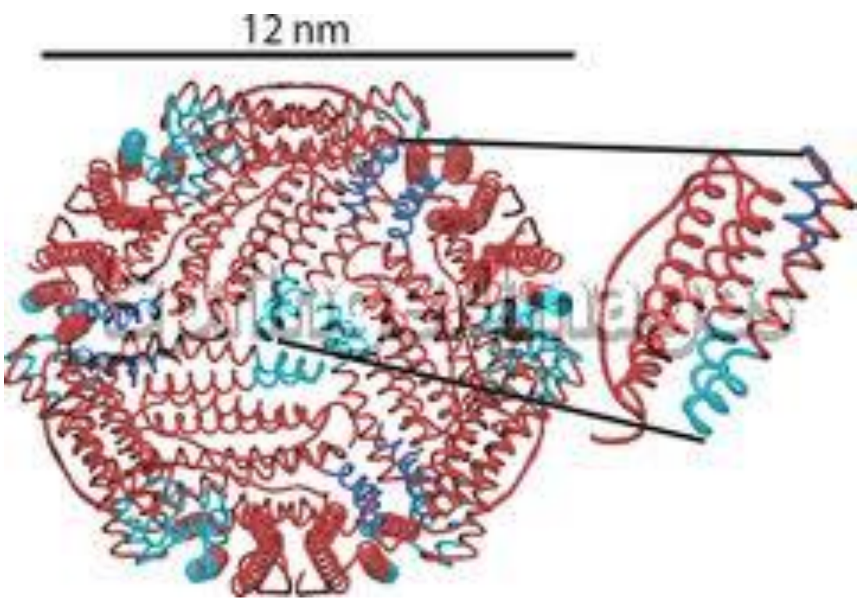
Iron storage in Ferritin



Of the 4 – 5 g Fe in the human body, up to half is stored within ferritin molecules.

This protein is made up of 24 subunits (or 12 dimeric units: i.e. the quaternary structure) which arrange to give a sphere of 12 nm diameter. This contains a cavity of 8 nm diameter for the storage of iron as an Fe(III) oxyhydroxide mineral.





The structure of the protein shell is well-studied and understood, as is the likely pathway for iron uptake. However, the nature of the mineral iron core and the mechanism for iron release are less well understood.

Respiration versus Photosynthesis

Respiration: $\{CH_2O\}_n + nO_2 \longrightarrow nCO_2 + nH_2O + \text{ENERGY}$

- Iron recycling is principally necessary in humans in order to utilise oxygen to burn carbohydrates – many of the other haem proteins mentioned simply deal with the dangerous oxygen-containing or free radical byproducts of this reaction.
- The process releases energy and water and carbon dioxide – both of which, but mostly CO_2, can be expelled via exhalation using the large gas-exchanging capabilities of the lungs (which also take up oxygen).
- CO_2 has to be transported efficiently to the lungs – otherwise any effort we make (even flexing our brain muscles) would make us explode as a result of the large amount of gas produced.
- The enzyme CARBONIC ANHYDRASE (CA) is able to "fix" the CO_2 in the form of bicarbonate (HCO_3^-) in order to transport the molecule in a soluble form thereby requiring far less volume.
- It is released and exhaled at the lungs as CO_2 and the whole process is completely reversible and one of the fastest enzymatic reactions known (essentially diffusion limited).
- This need to "solubulise" gas molecules is a special feature of biology – but note that we also learned to do this industrially for CO with the Mond process, fixing CO on Ni as $Ni(CO)_4$.
- How does CA work?

Carbonic Anhydrase – proposed mechanism of CO_2 recycling

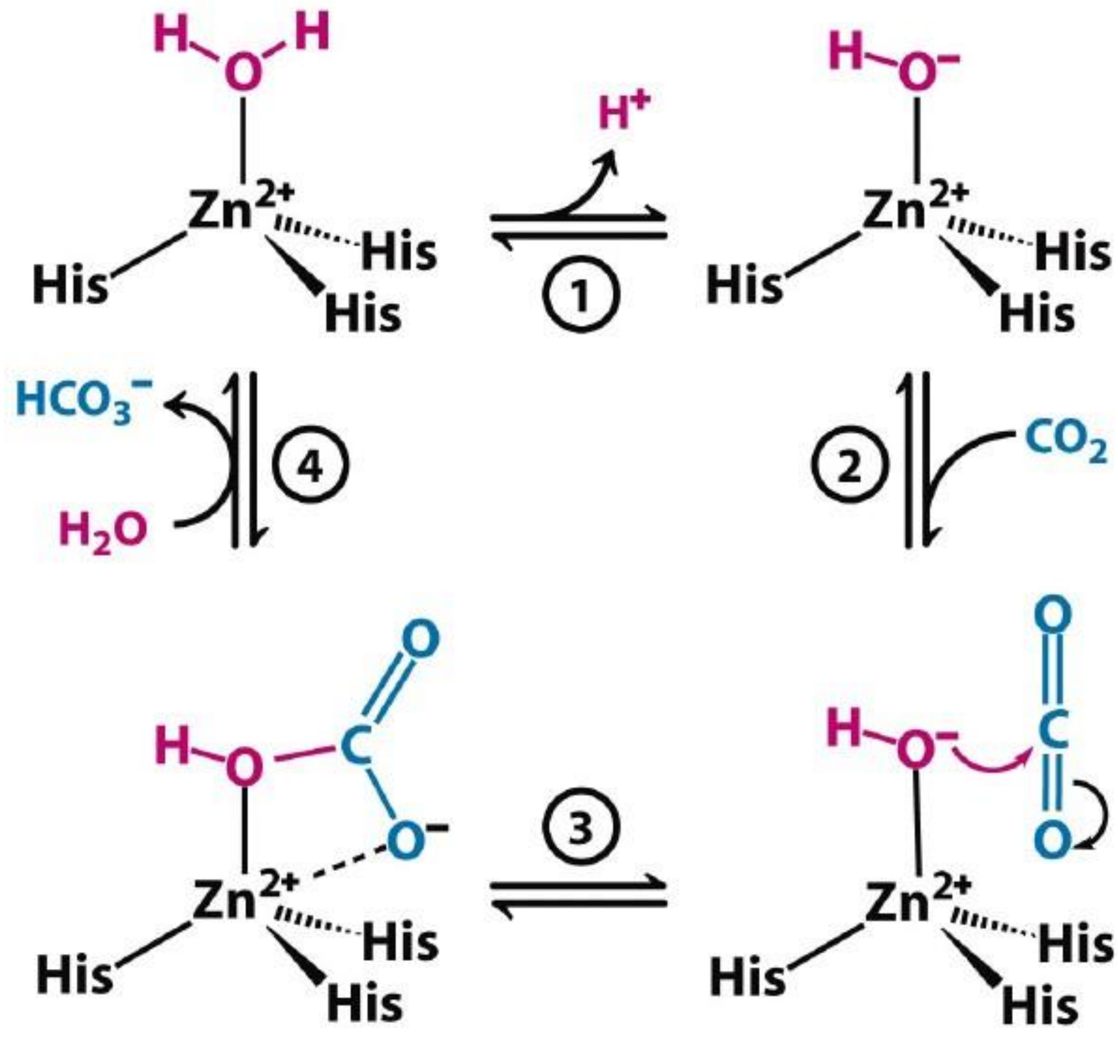


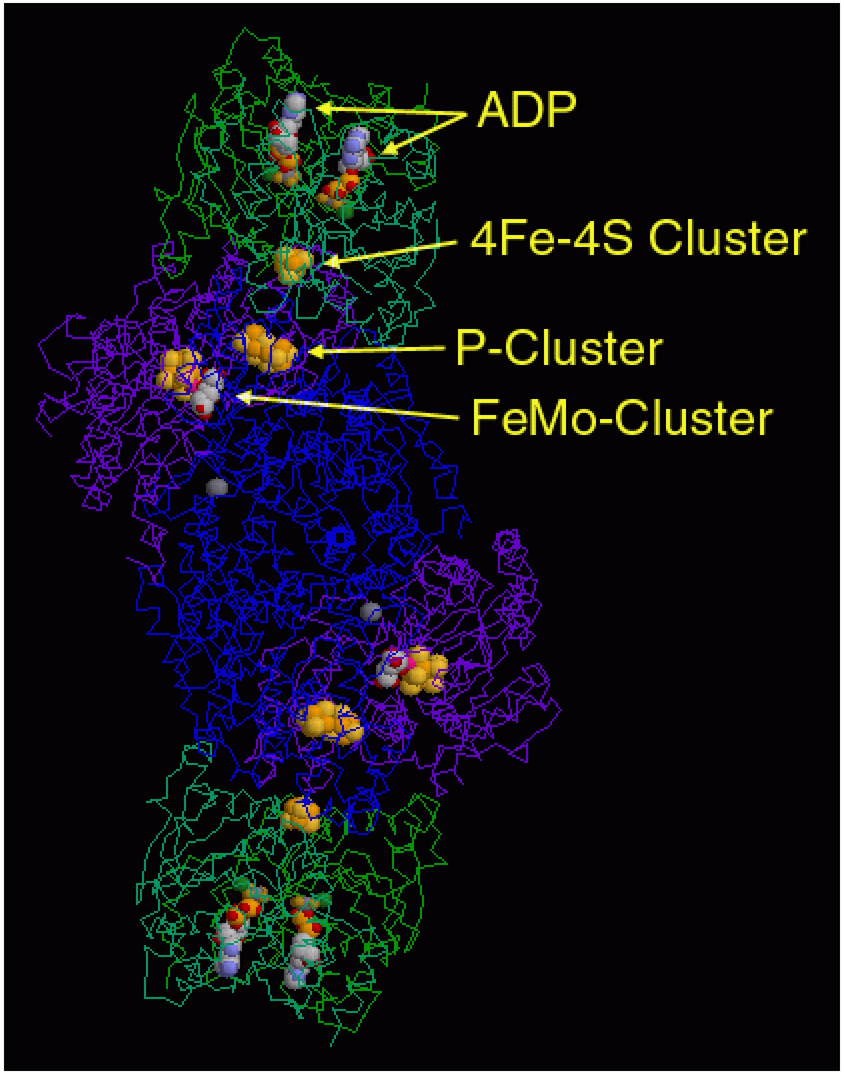
Figure 9-25
Biochemistry, Sixth Edition

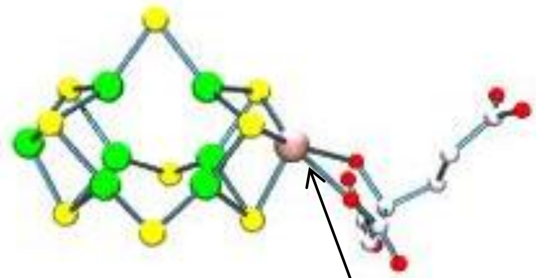
Biological nitrogen fixation

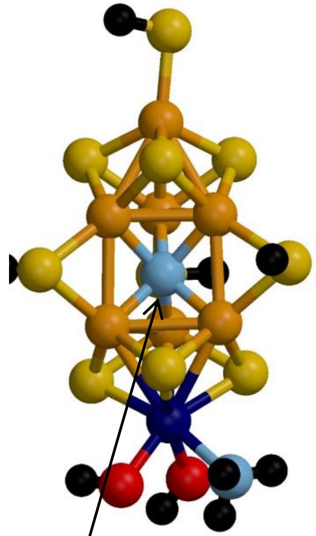
$$N_2 + 8\,H^+ + 8\,e^- + 16\,ATP \rightarrow 2\,NH_3 + H_2 + 16ADP + 16Pi$$

- Nitrogen-fixing bacteria take N_2 from the air under ambient conditions and combine this with protons essentially giving ammonia, NH_3.
- Nitrogen is now in its lowest oxidation state (-III) and can be incorporated into nitrogen-containing biomolecules and their building blocks such as amino acids and purine bases.
- The reaction is quantitative.
- The energy source needed to run the reaction and overcome the activation energy barrier is ATP.
- In addition, an enzyme containing an Fe/Mo cofactor – FeMoCo – is used.
- The structure of the catalytic core of this is of great interest for understanding better ways to fix nitrogen industrially than the Haber-Bosch process.

How biology fixes nitrogen







The successful crystallisation and structure solution of the nitrogenase cofactor system was a triumph. One surprise was that the Mo is bound by homocitrate and is not important for N_2 capture.

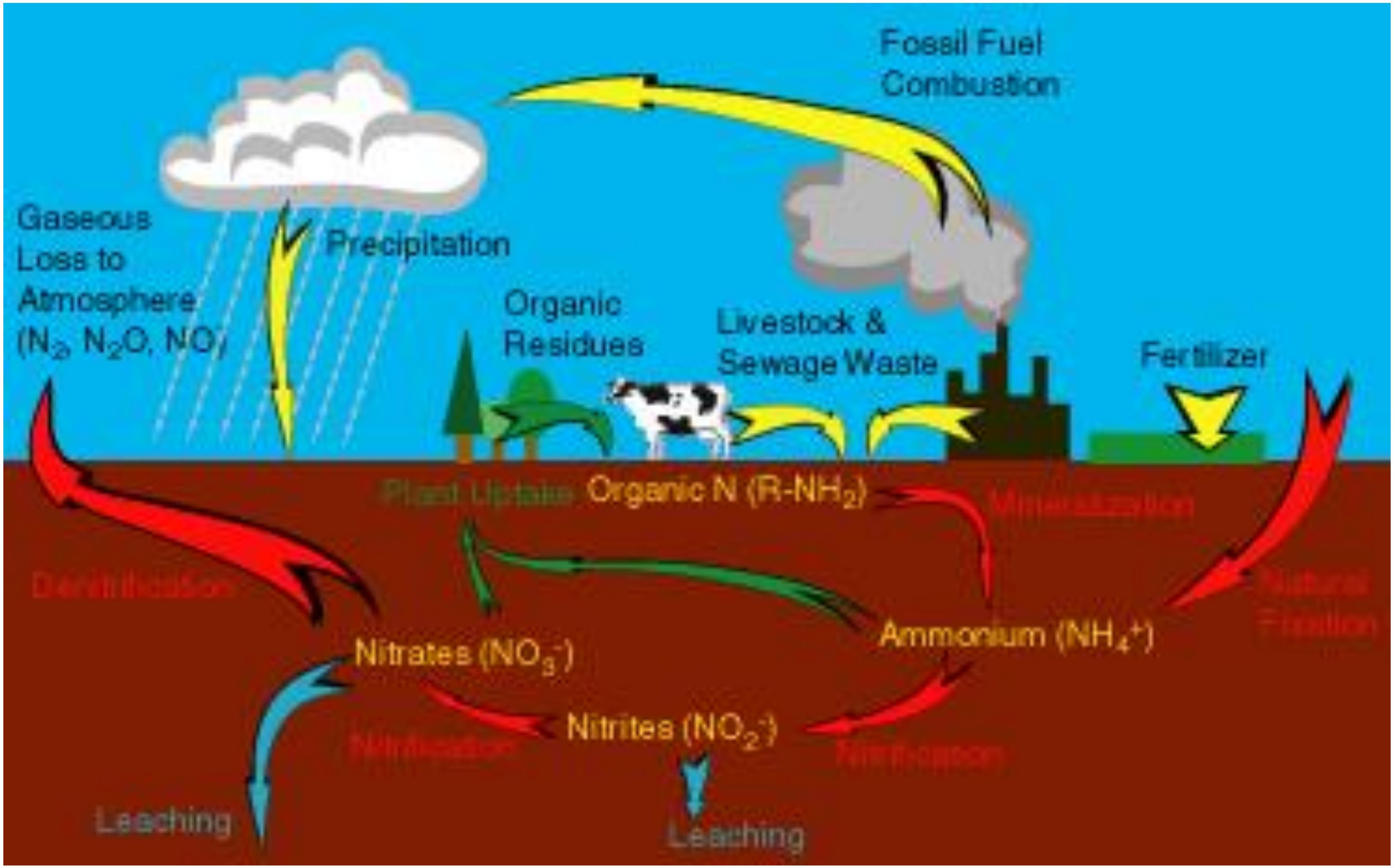
Initially, the core structure of metal centres at the heart of the FeMoCo was unusual (3-coordinate Fe(II) ions) until it was realised that there was a central, small atomic mass element anion such as carbide, nitride or oxide.

The "underlying" nitrogen fixing process has been manipulated by human activity for a long time

For centuries farmers have used crop rotation to nitrify the soil. By growing clover (see left) the nitrogen fixed by the bacteria in the root nodules can be incorporated into the soil, thereby allowing for increased production.

Currently, this "rotation farming" idea is bypassed and we simply spread N- (and P-) based fertilisers on the land to increase output.

The Nitrogen Cycle



Anthropogenic Nitrogen Fixation

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ (ΔH = −92.22 kJ/mol)

- Ammonia was first manufactured using the Haber process on an industrial scale in 1913 in BASF's Oppau plant in Germany.
- During World War I, the synthetic ammonia was utilised for the production of nitric acid for use in producing munitions. (No easily available source of “salpeter” otherwise).
- Note that fixing nitrogen is important for use in a variety of industrial processes such as the production of “Nylon” – polyamide – so not so different from reactions producing proteins as polypeptides. In the case of any polyamide there is one repeating unit and the material is a “synthetic silk” with the strands held together by hydrogen bonds as in a β-strand structure (i.e. as in the silk keratin proteins).
- However, fertiliser generated from ammonia produced by the Haber process is estimated to be responsible for sustaining one-third of the Earth's population.
- It is estimated that half of the protein within human beings is made of nitrogen that was originally fixed by this process; the remainder was produced by bacteria – see/hear BBC: Discovery - Can Chemistry Save The World? - 2. Fixing the Nitrogen Fix .

Anthropogenic Nitrogen Fixation

A historical (1921) high-pressure steel reactor for production of ammonia via the Bosch-Haber process on the premises of the University Karlsruhe (now KIT South Campus) Germany.

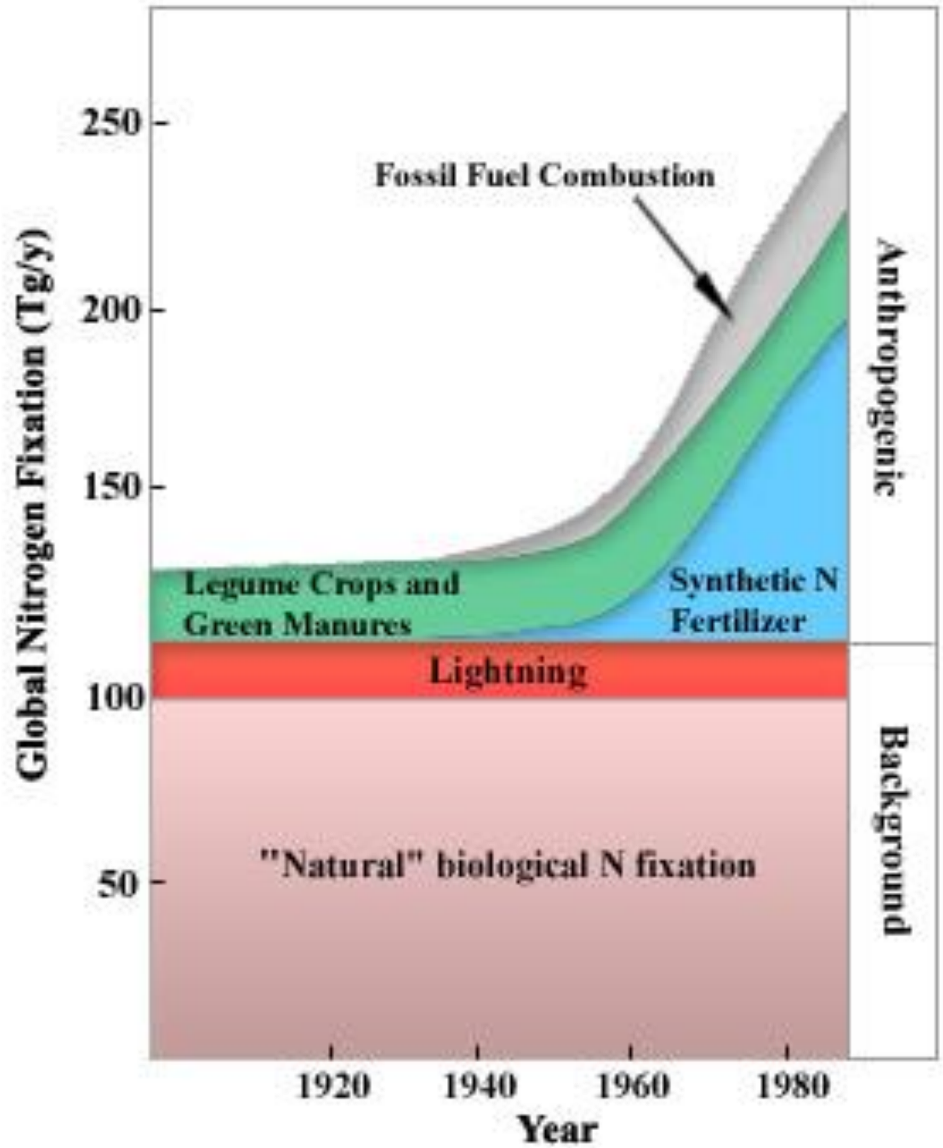
- Fritz Haber orchestrated the efforts to find a way to make ammonia out of its constituent elements and was awarded a Nobel prize in 1918.
- The reaction is thermodynamically favourable but kinetically blocked as a result of the extraordinary strength (nearly 1000 kJ/mol) of the N-N bond in N_2.
- In energy terms the reaction is extremely inefficient - it requires high pressures (expected from Le Chatelier) and high temperatures (against Le Chatelier) the latter required for the proper functioning of the catalyst (Swedish magnetite).
- Constant removal of product helps to increase overall yields of the reaction.
- It is an expensive process both in “real” monetary and environmental terms.

What Haber-Bosch has allowed us to do

According to the US EPA: http://cfpub.epa.gov/watertrain/pdf/issue1.pdf
We face the following scenario:

- Human activities during the past century have doubled the natural annual rate at which fixed nitrogen enters the land-based nitrogen cycle and the pace is likely to accelerate.
- This changes many things in the environment.
- In the atmosphere, concentrations of the greenhouse gas nitrous oxide and of the nitrogen precursors of smog and acid rain are increasing.
- Soils in many regions are being acidified and stripped of nutrients essential for continued fertility.
- The waters of streams and lakes in these regions are also being acidified.
- Excess nitrogen is being transported by rivers into estuaries and coastal waters.
- It is quite likely that this unprecedented nitrogen loading has already contributed to long-term declines in coastal fisheries and accelerated losses of plant and animal diversity in both aquatic and land-based ecosystems.

How are we affecting the amount of available nitrogen?

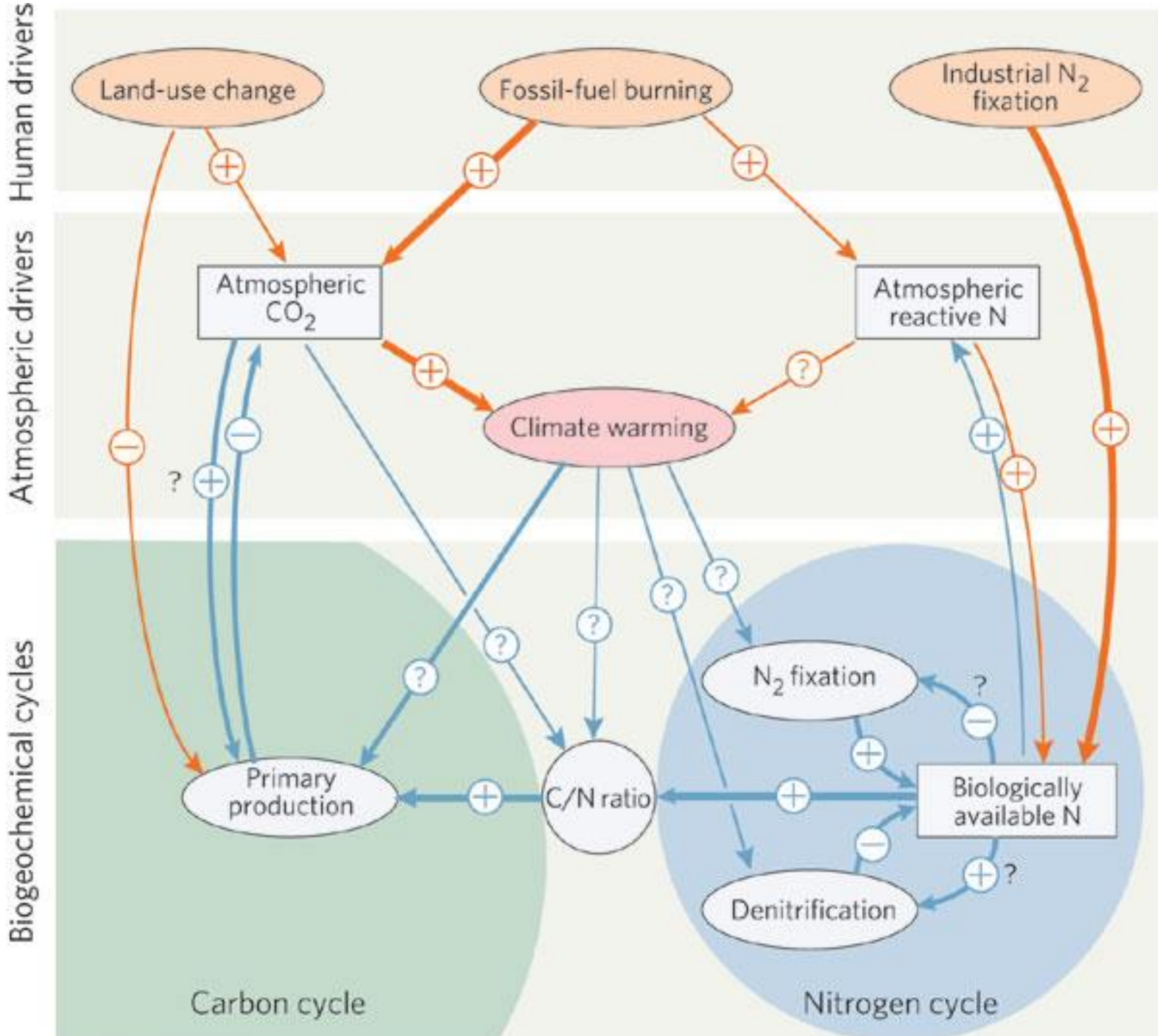


Recent increases in anthropogenic N fixation in relation to "natural" N fixation. Modified from Vitousek, P. M. and P. A. Matson (1993). Agriculture, the global nitrogen cycle, and trace gas flux. The Biogeochemistry of Global Change: Radiative Trace Gases. R. S. Oremland. New York, Chapman and Hall: 193-208.

As the anthropogenic contribution to "available N" we can identify **agricultural**, **industrial** and **aquacultural** contributions.

These are obviously increasing at an alarming rate.

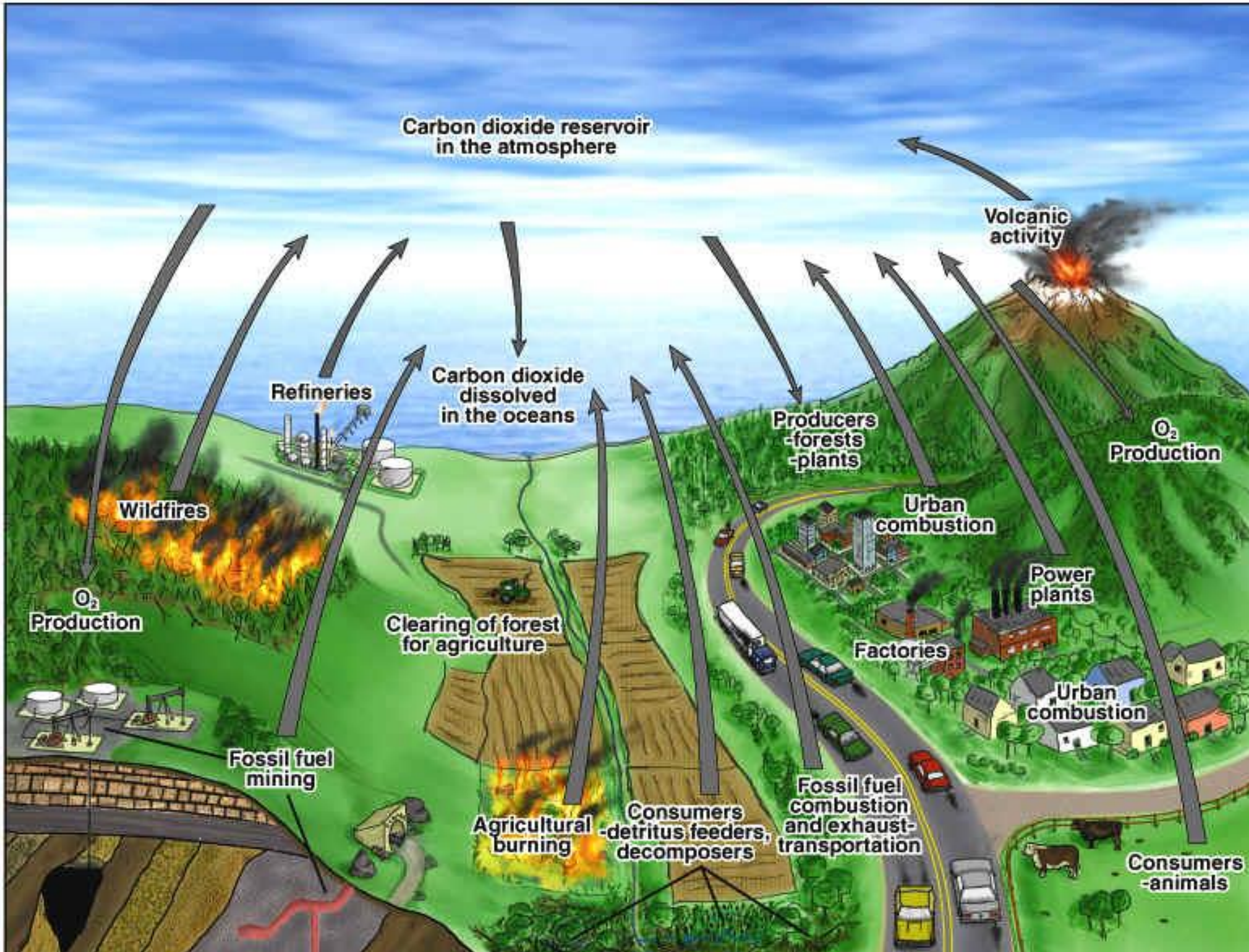
Interplay of the N and C cycles



The main anthropogenic drivers of these interactions during the twenty-first century are shown. Plus signs indicate that the interaction increases the amount of the factor shown; minus signs indicate a decrease; question marks indicate an unknown impact (or, when next to a plus or minus sign, they indicate a high degree of uncertainty). Orange arrows denote the direct anthropogenic impacts, and blue arrows denote natural interactions, many of which could also be anthropogenically modified. Arrow thickness denotes strength of interaction. Only selected interactions are shown.

Nature **451**, 293-296 (17 January 2008) doi:10.1038/nature06592; Published online 16 January 2008

Combined Carbon/Oxygen Cycle



Selected examples of the power of coordination clusters in biology

Haemoglobin – supramolecular mononuclear Fe units improve efficiency of oxygen uptake and transport

Ferritin – supramolecular ligand shell (protein subunits) produce an ideal cavity to capture nanoscale iron(III) oxyhydroxide

Nitrogenase – constellation of metal ions allows fixation of nitrogen at ambient pressure and temperature with high turnover and yield of reduced N oxidation states

PSII – concerted interplay of ligand shell, supramolecular environment and Mn4Ca coordination cluster core enable water splitting to deliver protons for carbohydrate manufacture (energy storage) and byproduct of oxygen

Coordination clusters in Biology: Photosynthesis and Photosystem II

The process of photosynthesis uses light energy to convert water and CO_2 into carbohydrates with oxygen as a byproduct:

$$H_2O + CO_2 \longrightarrow \{CH_2O\}_n + nO_2$$

Within Photosystem II (PSII) the water splitting reaction takes place:

$$2H_2O \longrightarrow 4H^+ + 4e + O_2$$

Coordination clusters in Biology: Photosynthesis and Photosystem II

- Understanding how the water is split has been the subject of intensive research.
  - In the natural system the overall reaction of photosynthesis shows how the sun's energy can be stored in the form of carbohydrates. We gain energy from this source through consumption as food and consumption as fossil fuels. A result of this is the production of carbon dioxide – ideally we just need to keep the balances right. Unfortunately, we are out of balance.
  - Artificially we hope we could use the water splitting reaction to provide H_2 for use as a fuel.

What is established?

Coordination clusters in Biology: Photosynthesis and Photosystem II

- Before the crystal structure was available, it had been established that a manganese containing complex was responsible for the catalytic conversion of water into protons, electrons and oxygen.
- It was established that four pulses of light were needed pumping out four electrons and four protons plus the byproduct oxygen
- Kok proposed a cycle describing this process with five S states
- It appeared that at some or all stages of the cycle calcium and chloride ions were important. Azide could act as an inhibitor

The KOK cycle

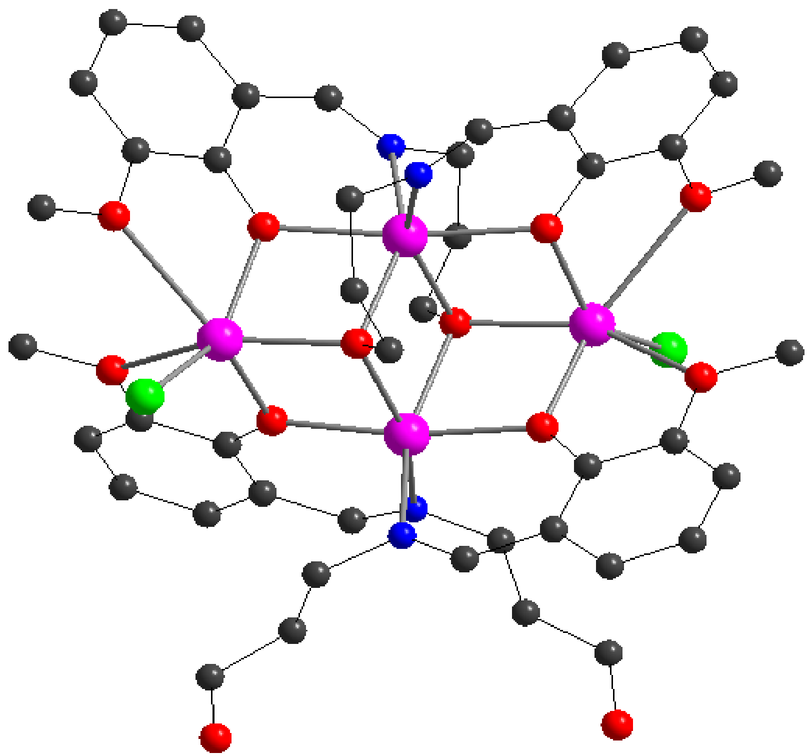
Kok states and possible oxidation states of the 4 Mn. Note that there is no consensus on oxidation states even for S0 state!

S0:	II, III, III, III	
	II, III, IV, IV	1 photon in, 1e and 1 H^+ out.
	III, III, III, IV	
S1:	III, III, III, III	1 photon in, 1e and 1 H^+ out.
	III, III, IV, IV	
S2:	III, III, III, IV	1 photon in, 1e and 1 H^+ out.
	III, IV, IV, IV	
S3:	III, III, IV, IV	1 photon in, 1e and 1 H^+ out.
	IV, IV, IV, IV	Electron via radical?
S4:	III, III, IV, IV	Return to S0 on production of O_2.
	IV, IV, IV, IV	Add 4e and then $2H_2O$.

Model studies

- The goal of the model compound studies before any protein crystallographic data were available was mainly to provide structural models.
- Most workers aimed to synthesise tetramanganese clusters with Mn in various oxidation states.
- Variations on cubane, tetrahedral and butterfly motifs were produced.
- No real consensus on best model but lots of fascinating Mn chemistry was developed.
- Features to model include electronic structure.
- Some functional models were also produced.

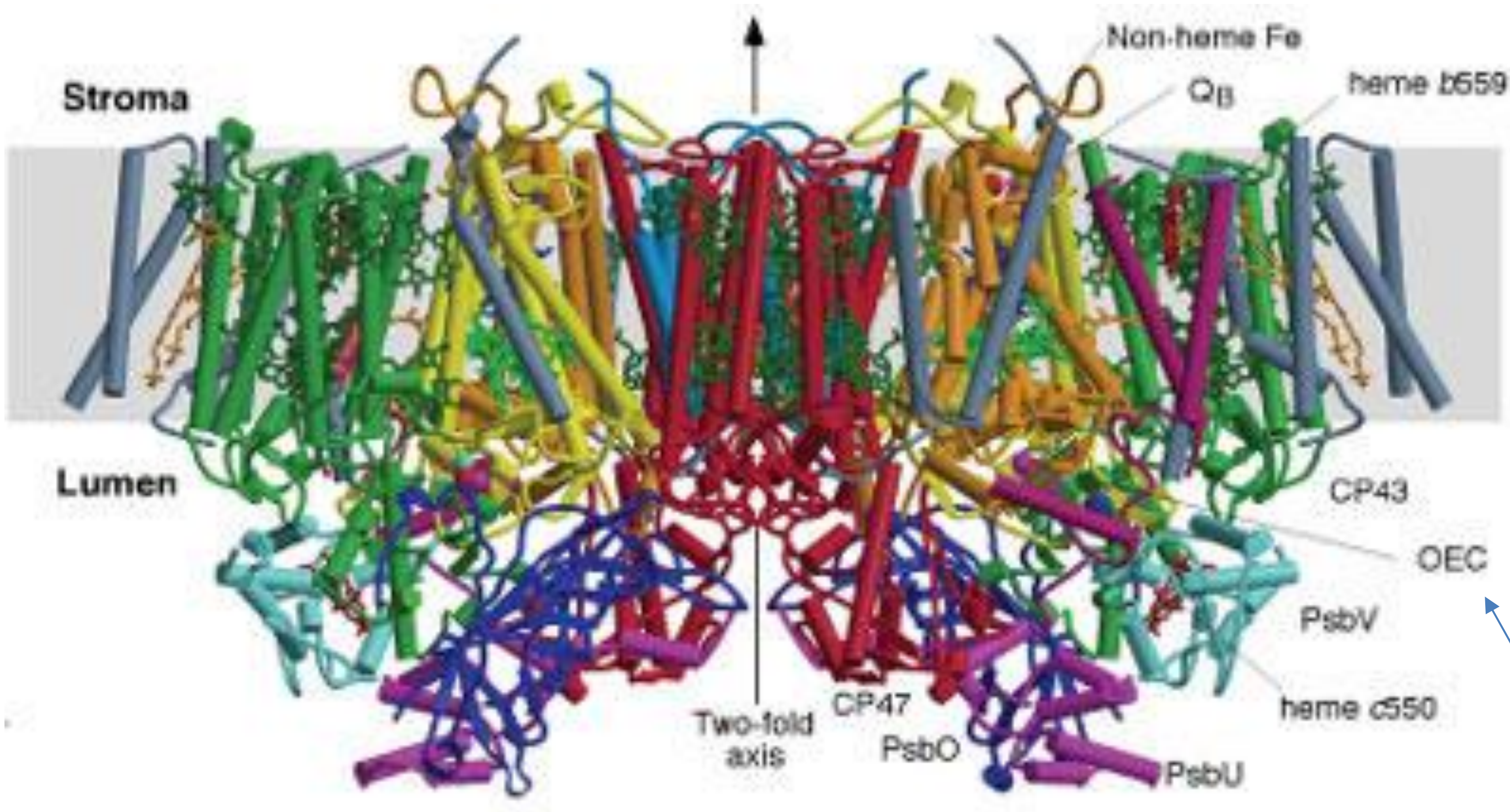
An example of a butterfly core model: $[Mn^{II}_4(L_2)(HL)_2Cl_2]$



Schiff base ligands are useful since they are easily functionalised and can stabilise Mn(II), Mn(III) and Mn(IV) states.

I.J. Hewitt, J-K. Tang, N.T. Madhu, C.E. Anson, A.K. Powell

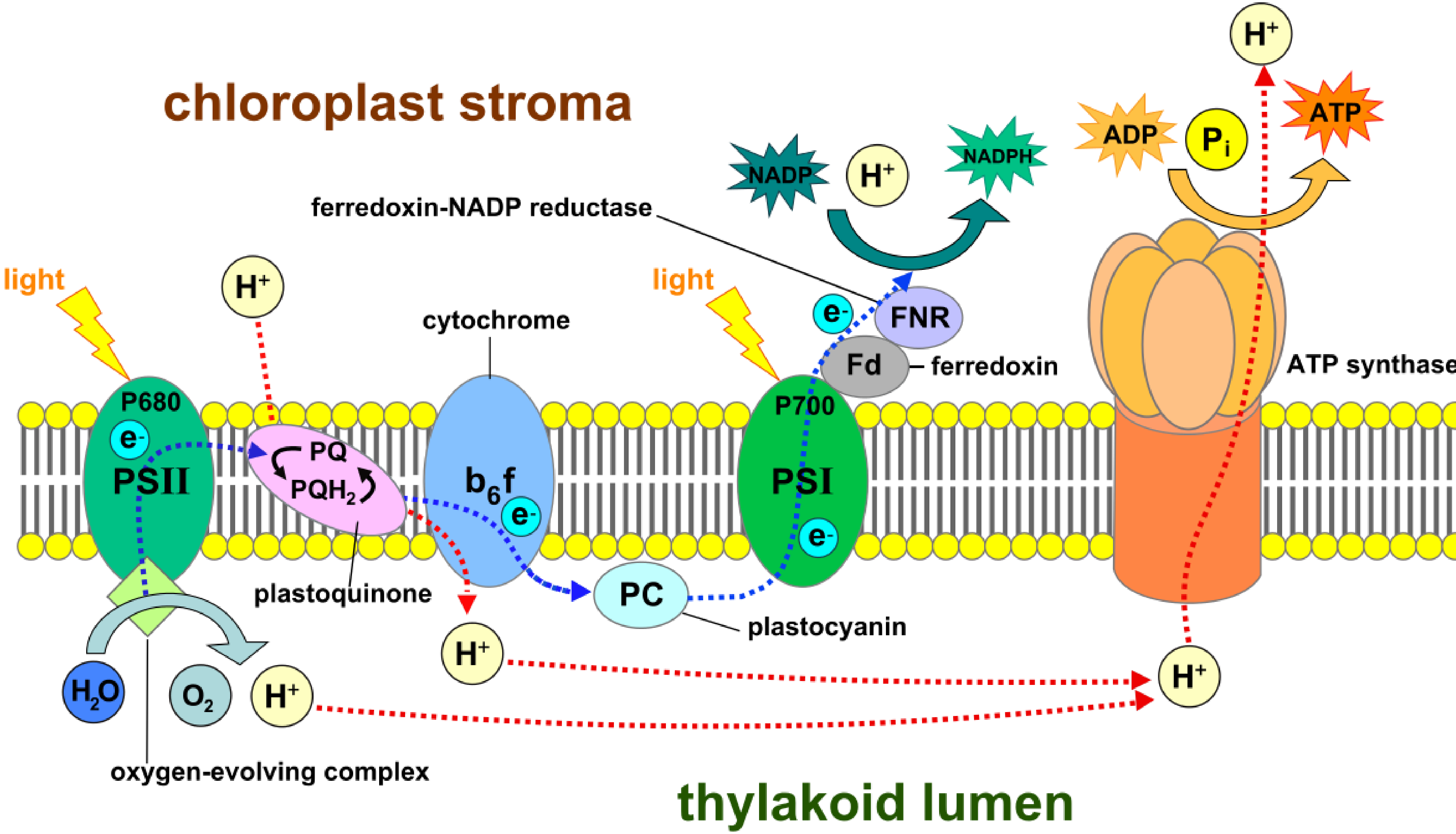
Protein structure of Photosynthetic apparatus PSII



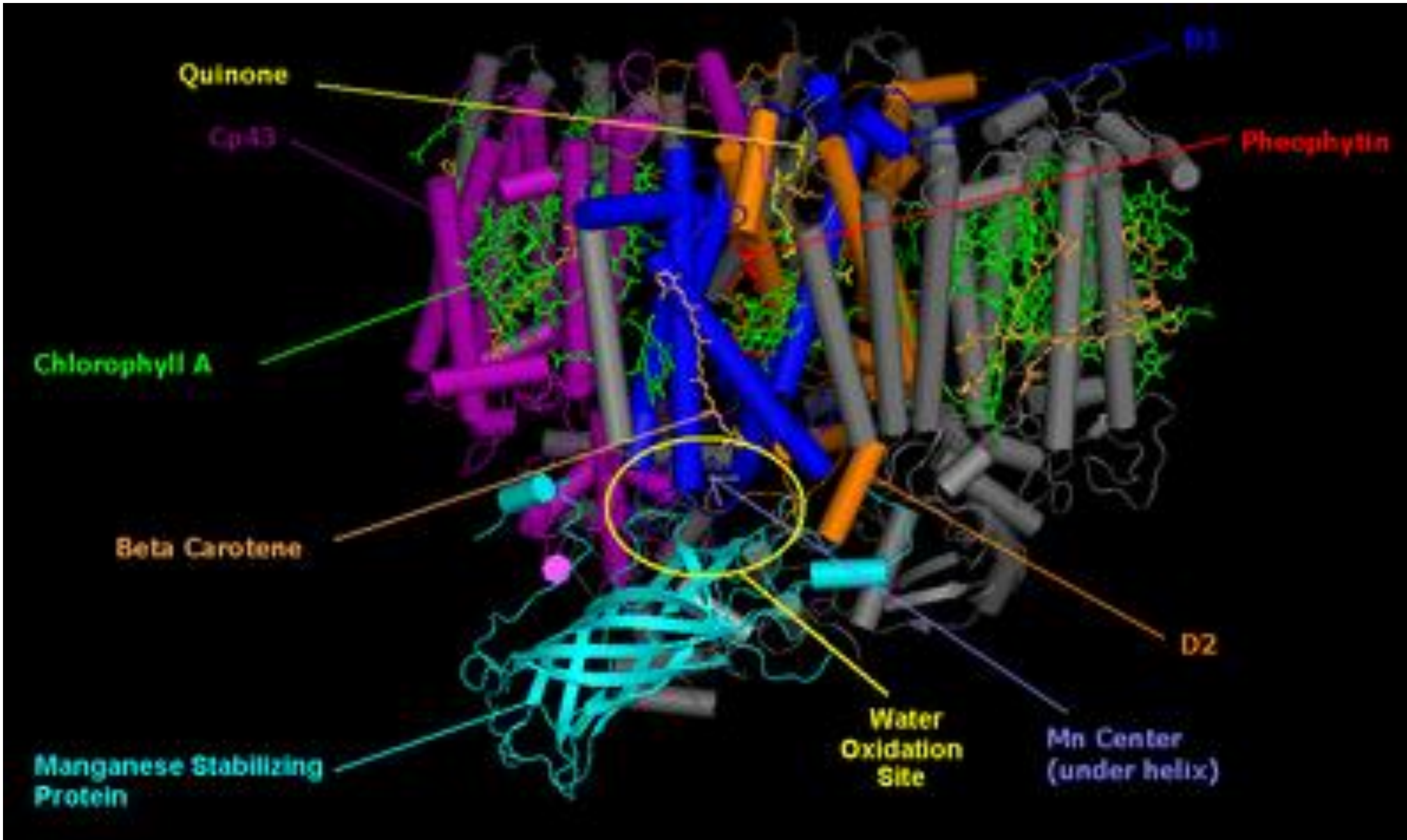
Note how small the OEC is…

K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber, S. Iwata, Science, 2004, 303, 1831

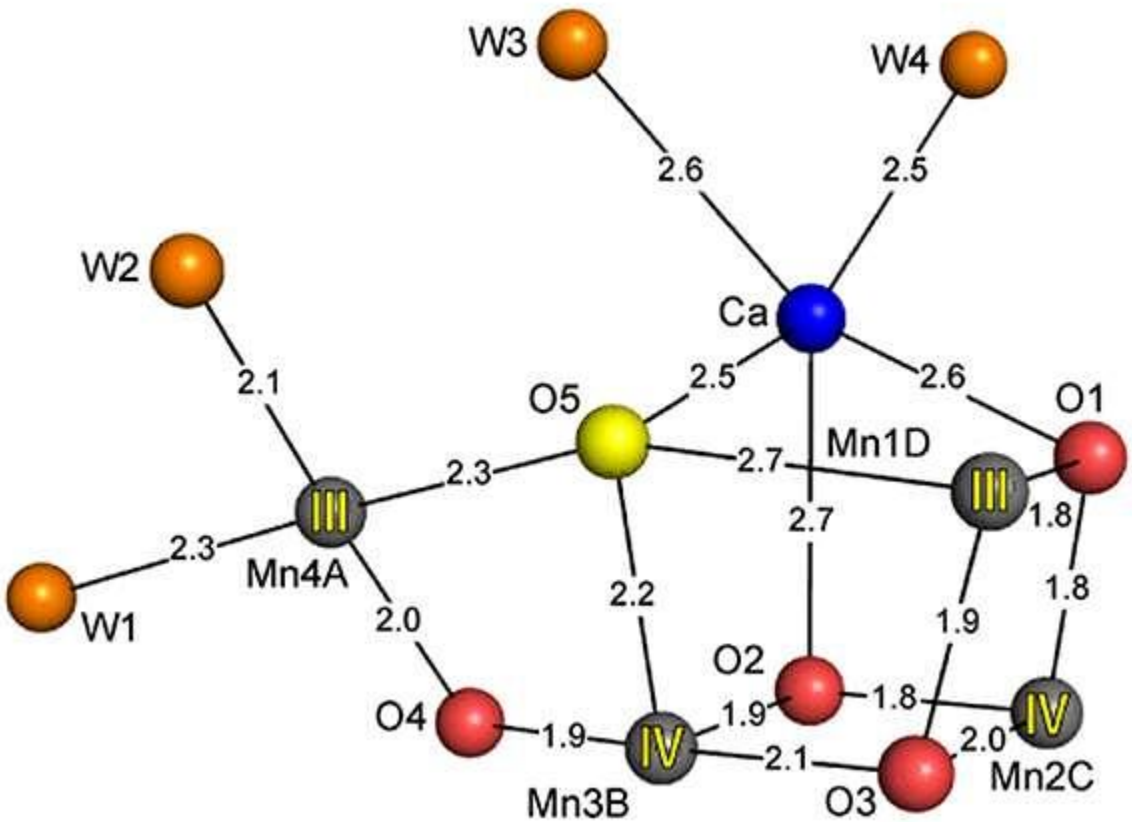
The complete process is quite involved…



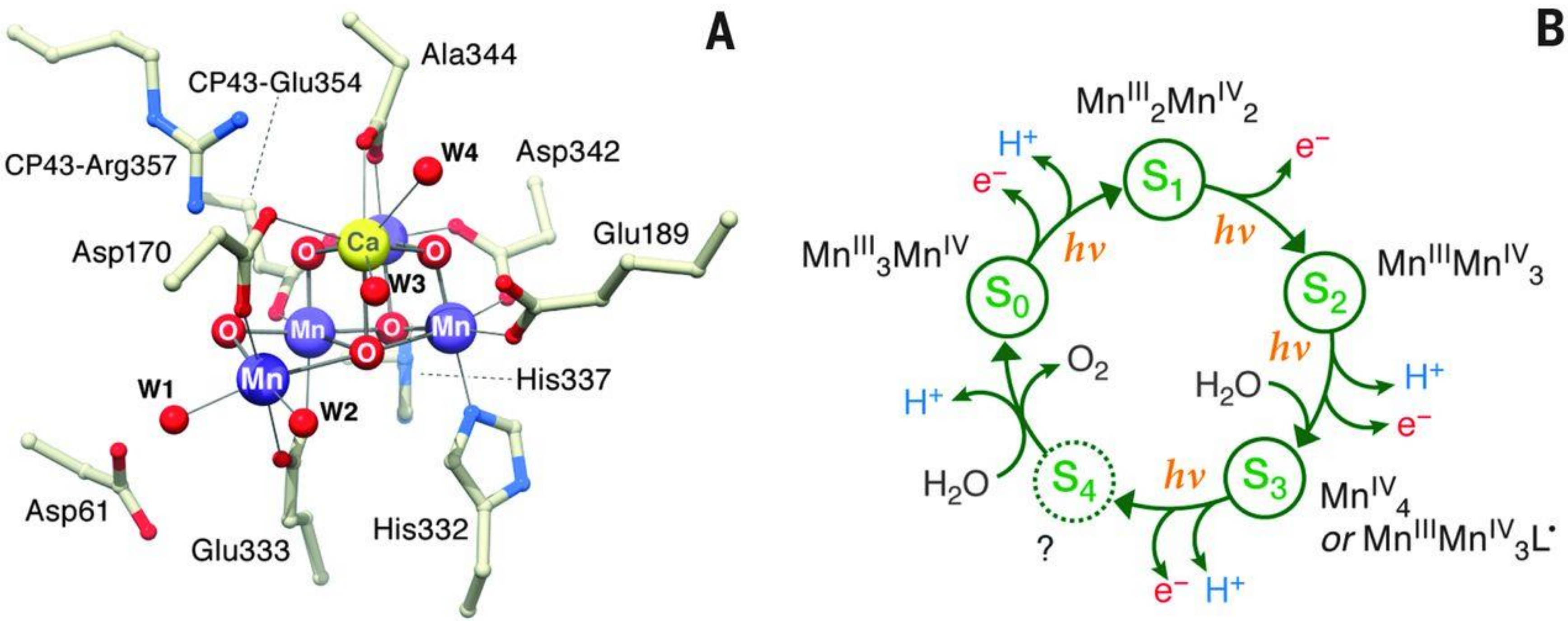
Many components working together in the complete system



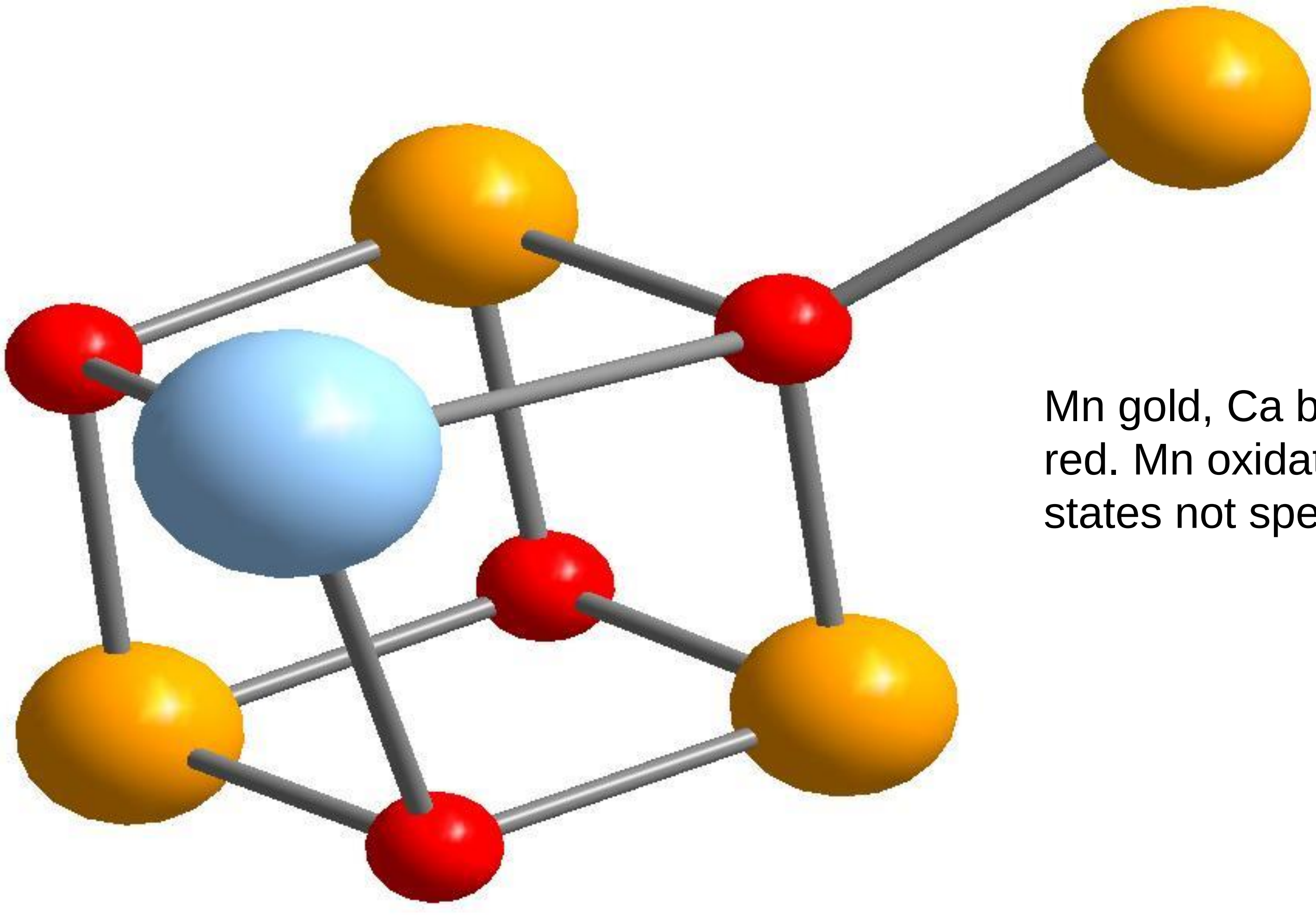
Current best guess for the oxidation states of Mn in the OEC resting (S0) or S2 state



Current view of how the Mn_4Ca cluster might look (A) and what the oxidation states might be for S_0 to S_4 in the Kok cycle (B)

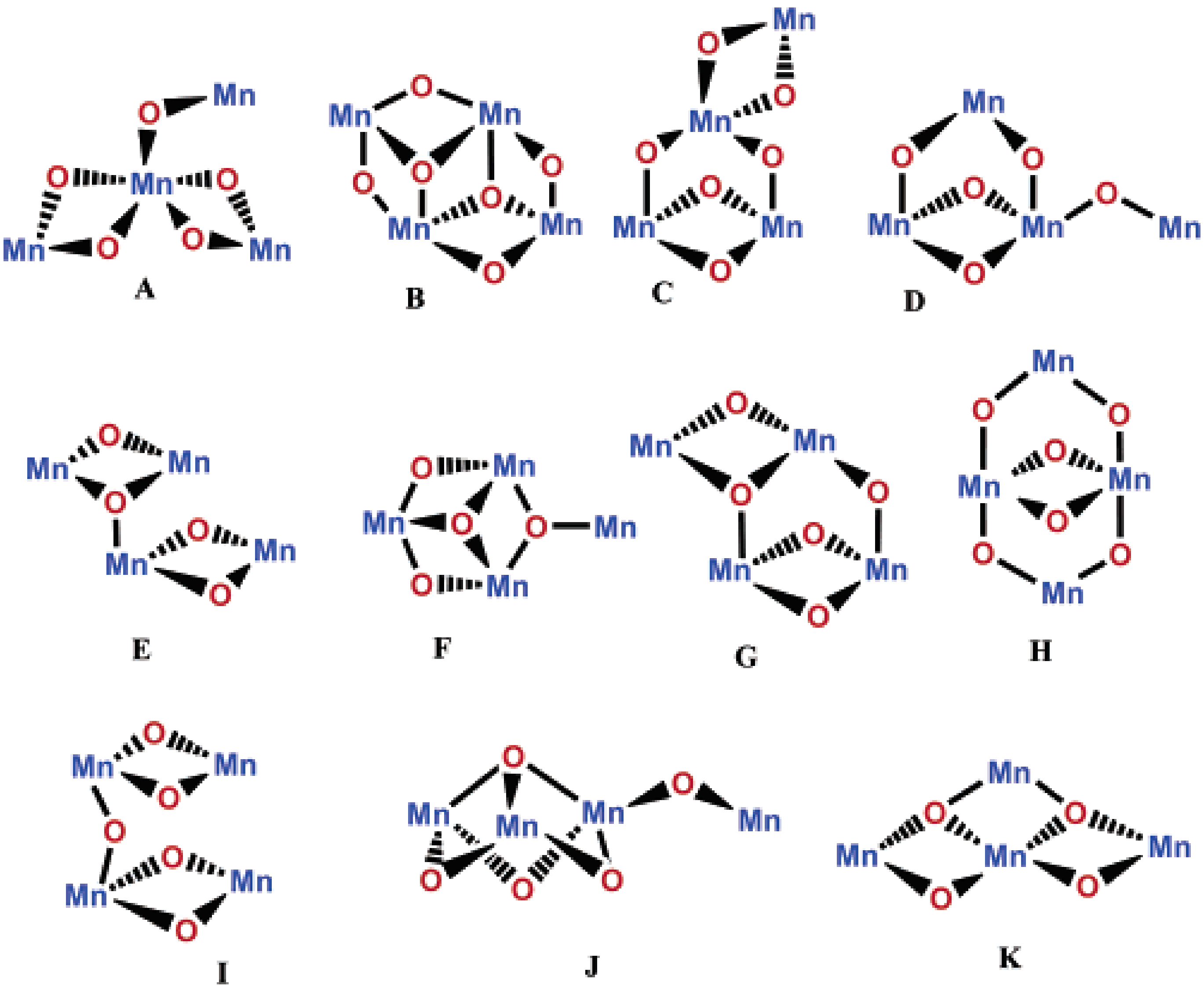


The new goal for new model compounds?



Mn gold, Ca blue, O red. Mn oxidation states not specified.

A big problem is the arrangement of the Mn centres and how they are connected (oxygen bridges – oxide or hydroxide?)

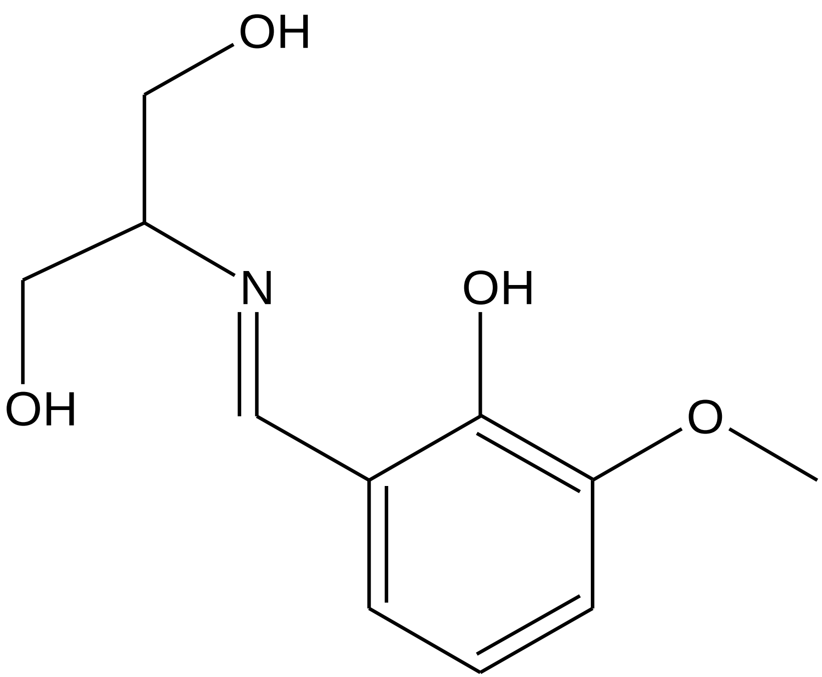


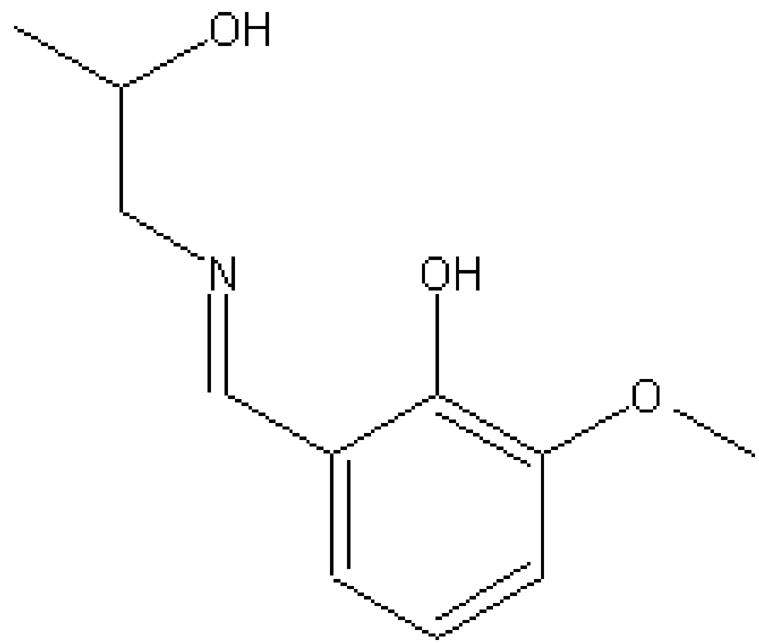
Some suggestions based on EXAFS, magnetic data etc.

Note oxidation states not given. Problems with radiation damage have been identified

New model compounds

We found that a range of Mn4 compounds was accessible using these related Schiff base ligands prepared by condensing *o*-vanillin and the appropriate ethanolamine:





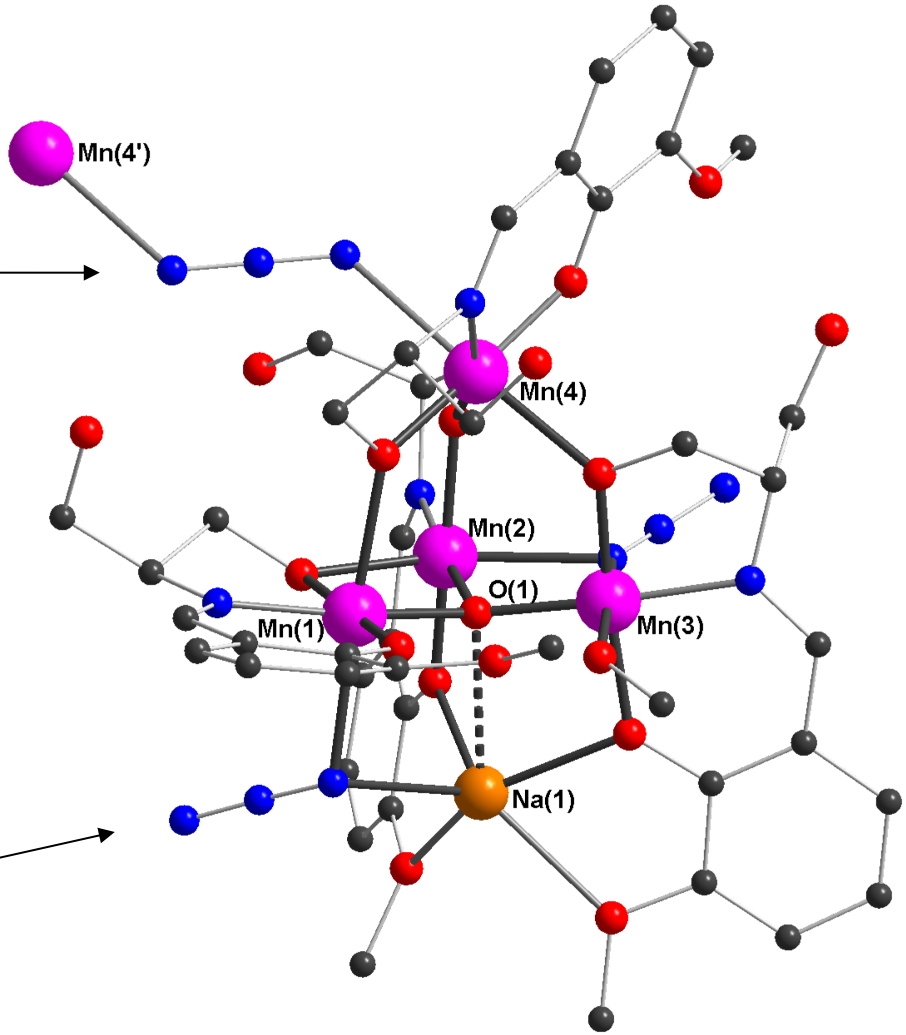
I. J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C. E. Anson, A. K. Powell, Chem. Commun., 2006, 2650 - 2652

We found a NaMn4 motif in an aggregate system.

Azide link to another unit

$[NaMn^{III}_4(\mu_3\text{-}O)]$ core

Note bridging azides

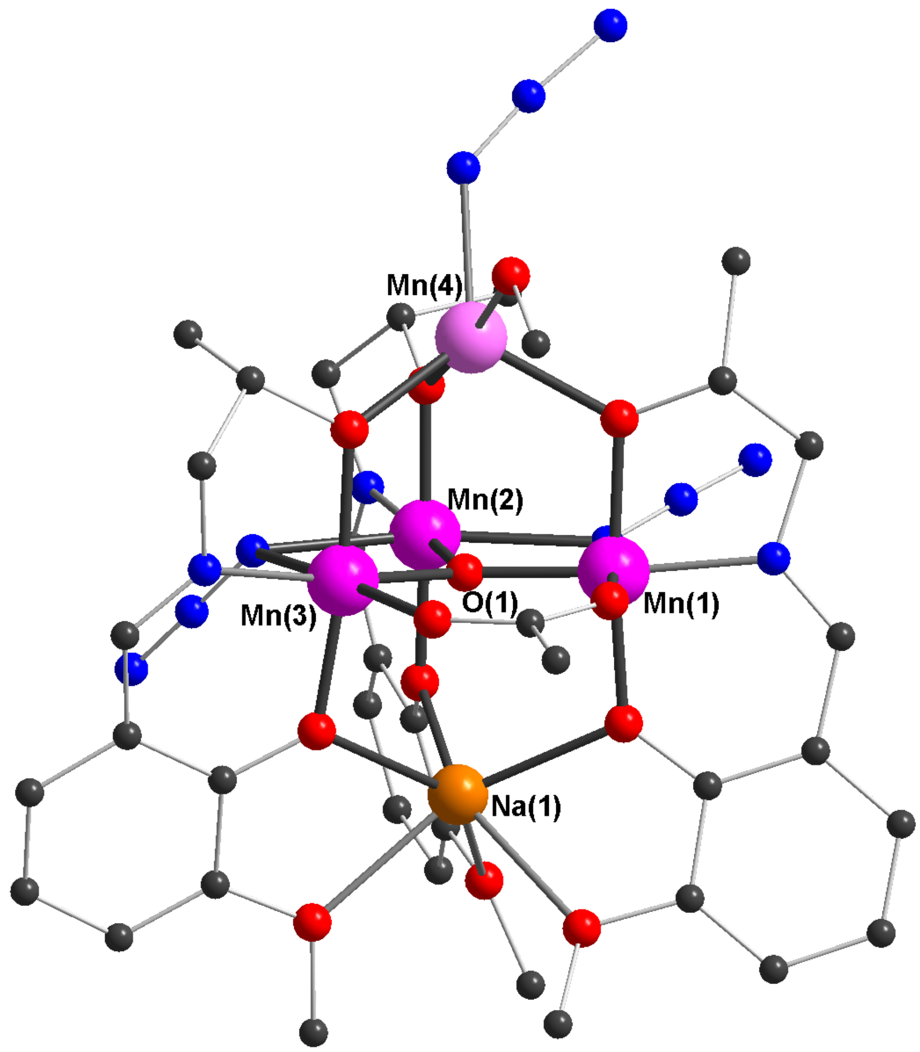


I. J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C. E. Anson, A. K. Powell, Chem. Commun., 2006, 2650 - 2652

Using the other Schiff base also leads to a NaMn4 motif.

$[NaMn^{III}{}_3Mn^{II}(\mu_3\text{-}O)]$ core

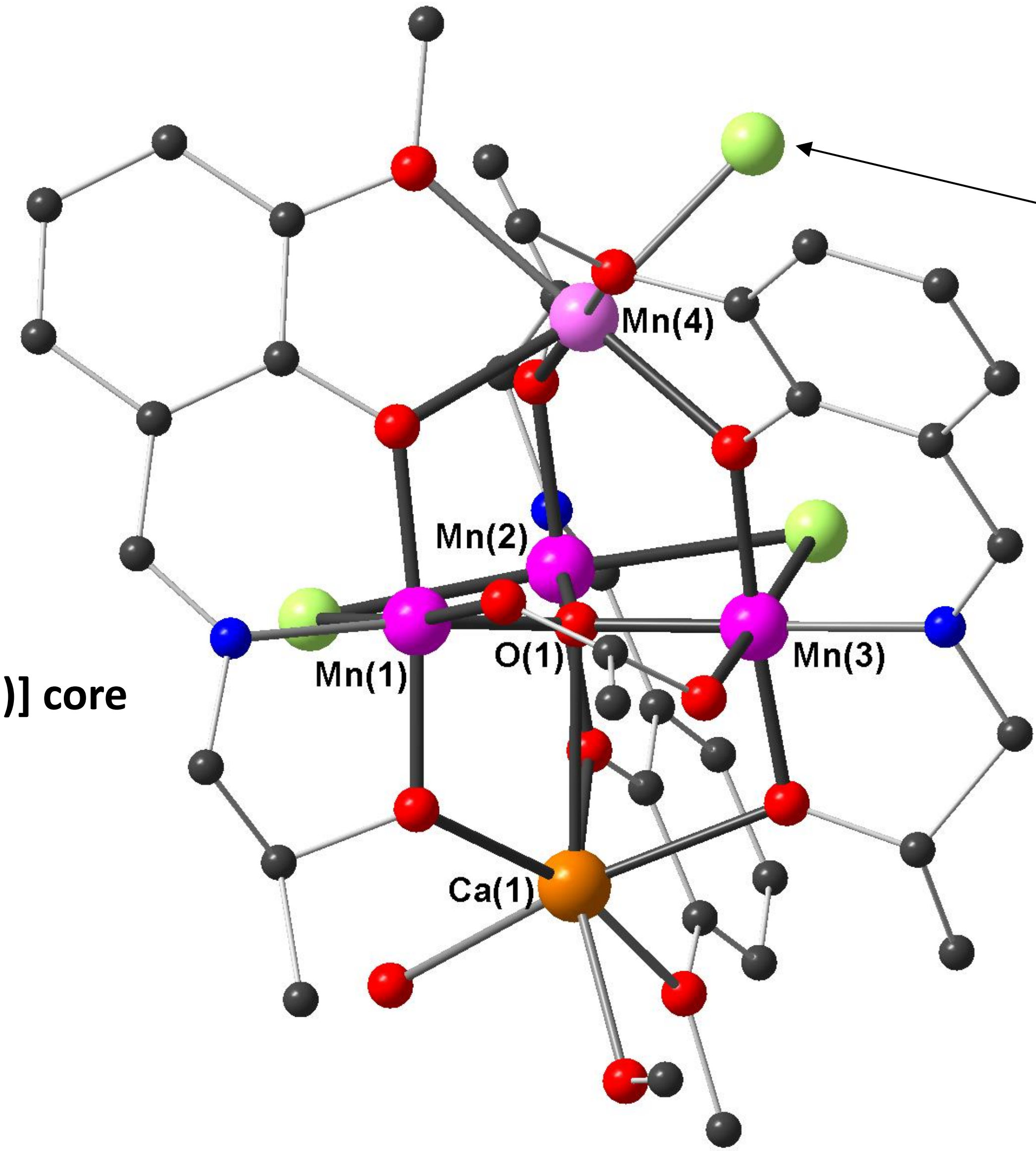
Can we replace Na?



I. J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C. E. Anson, A. K. Powell, Chem. Commun., 2006, 2650 - 2652

YES – with Ca!

The most realistic model so far?



Note chloride ligands

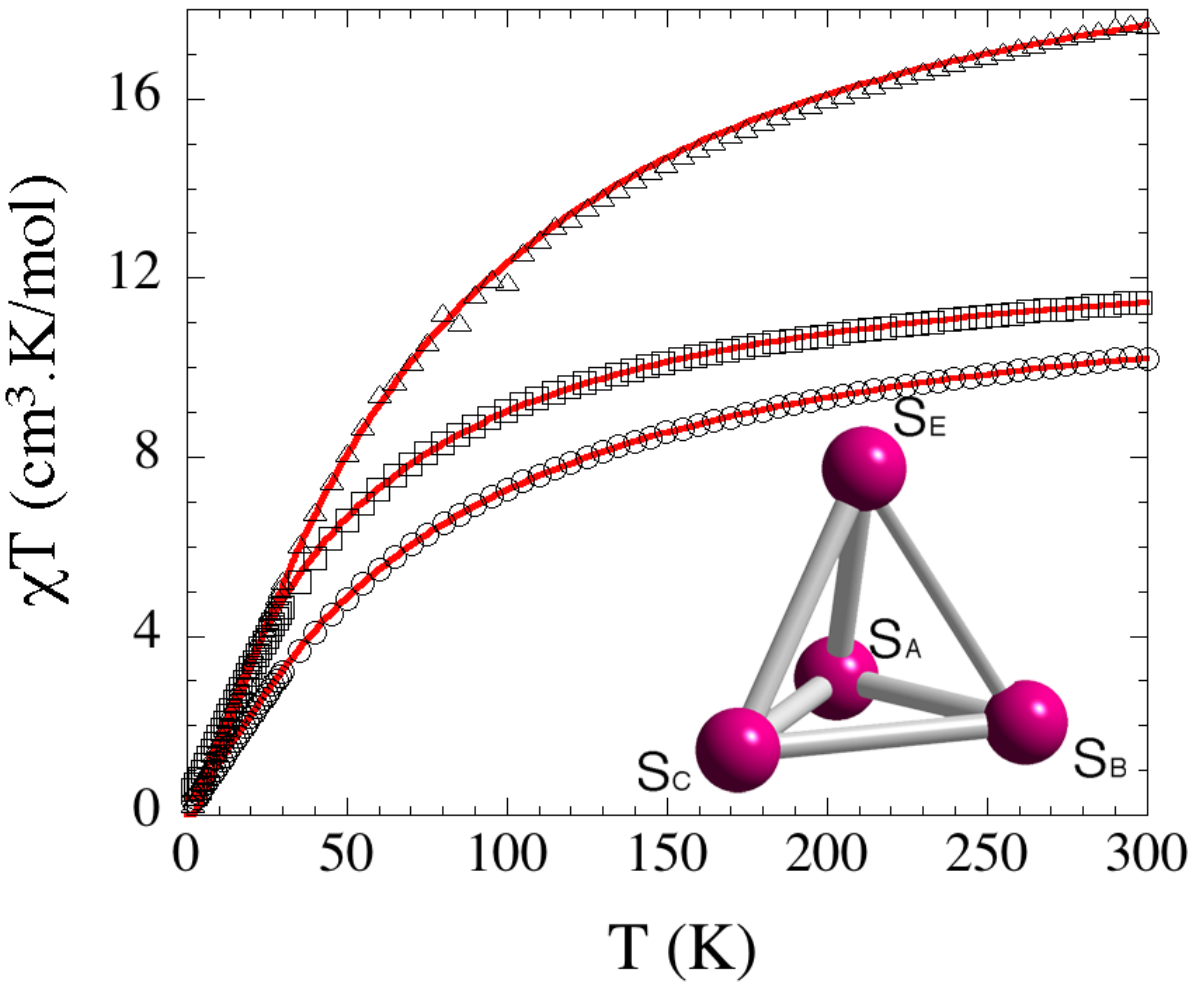
$[CaMn^{III}_3Mn^{II}(\mu_4\text{-}O)]$ core

Oxidation states and positions of metals?

I. J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C. E. Anson, A. K. Powell, Chem. Commun., 2006, 2650 - 2652

Magnetic susceptibility studies

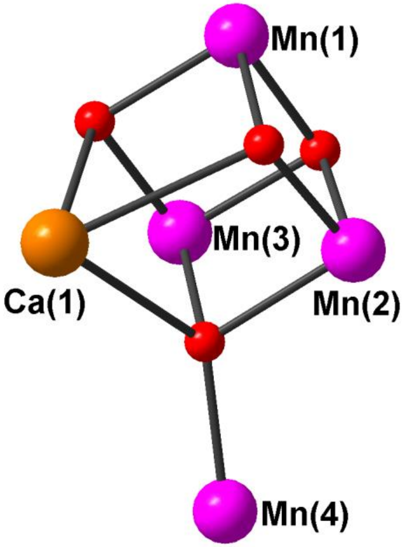
Magnetic data for the 3 compounds indicate the Mn^{III}_4 aggregate (triangles) has an S = 0 ground state, the other two S = ½. Here the data are fit using a simplified spin model, subsequently a broken symmetry DFT/CASCI study accounts for all interactions.

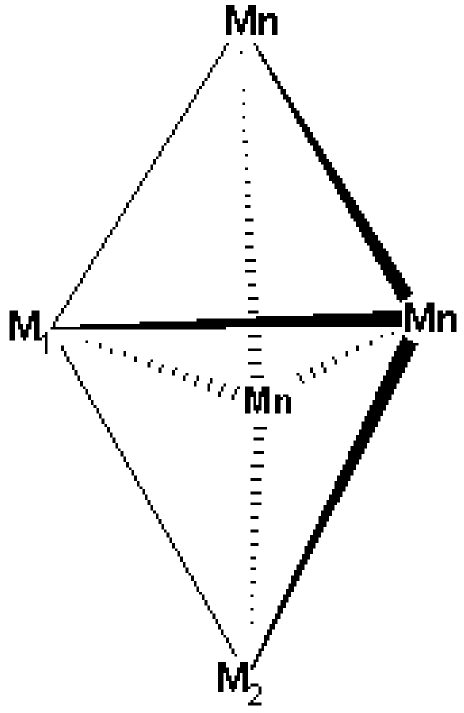


This can be favourably compared with studies on S0 and S1 states

I. J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C. E. Anson, A. K. Powell, Chem. Commun., 2006, 2650 – 2652; H. Fliegl, K. Fink, W. Klopper, C. E. Anson, A. K. Powell, R. Clérac, Phys. Chem. Chem. Phys, 2009, 11, 3900-3909

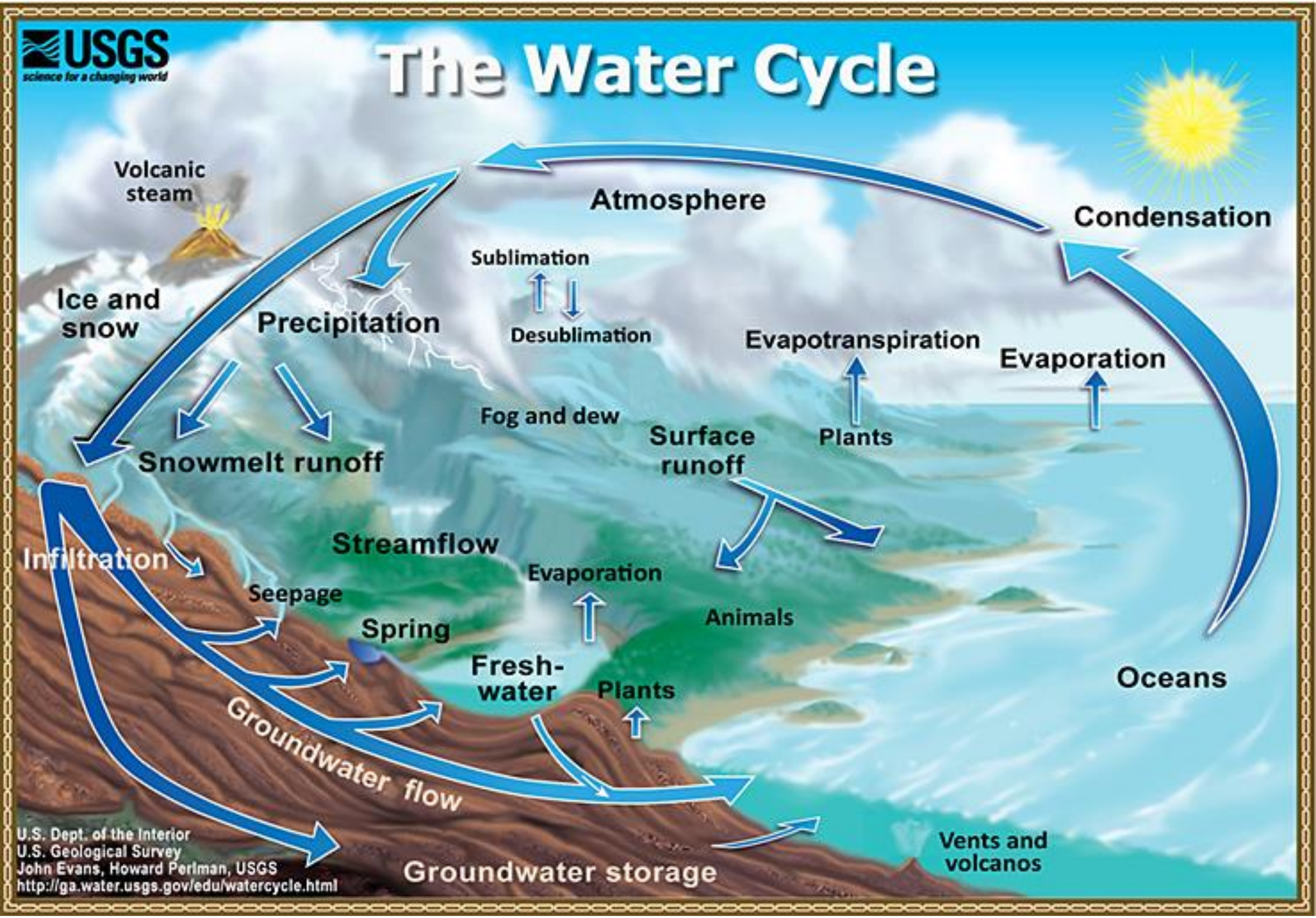
Comparison of the suggested arrangement of metals in the OEC and the models





Compound	M1	M2
1, 2	Mn	Na
3	Mn	Ca
OEC	Ca	Mn

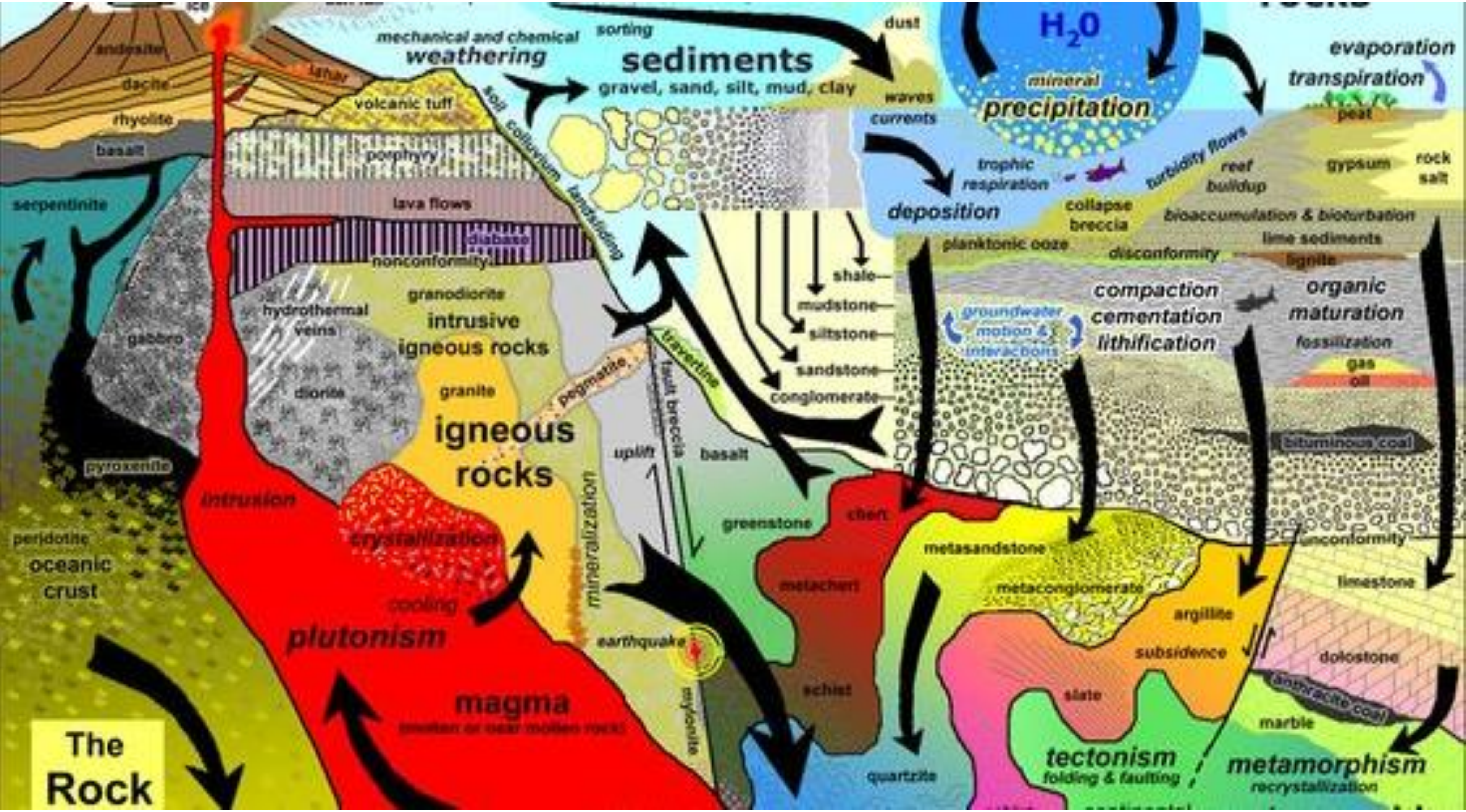
I. J. Hewitt, J.-K. Tang, N.T. Madhu, R. Clérac, G. Buth, C. E. Anson, A. K. Powell, Chem. Commun., 2006, 2650 - 2652


USGS
science for a changing world
The Water Cycle
Volcanic steam
Atmosphere
Condensation
Sublimation
Desublimation
Ice and snow
Precipitation
Evapotranspiration
Evaporation
Fog and dew
Surface runoff
Plants
Snowmelt runoff
Streamflow
Infiltration
Evaporation
Seepage
Spring
Animals
Fresh-water
Plants
Oceans
Groundwater flow
U.S. Dept. of the Interior
U.S. Geological Survey
John Evans, Howard Perlman, USGS
http://ga.water.usgs.gov/edu/watercycle.html
Groundwater storage
Vents and volcanos

Rock Cycle

- The rock cycle is the set of processes by which earth materials change from one form to another over time.
- The concept of uniformitarianism, which says that the same earth processes currently at work have occurred throughout geologic time, helped develop the idea of the rock cycle in the 1700s.
- Processes in the rock cycle occur at many different rates.
- The rock cycle is driven by interactions between plate tectonics and the hydrological cycle.
- Distinguish between igneous, sedimentary and metamorphic rocks.
- Consider rocks which form in abundance as a direct result of the presence of life – we can think of these as biogenic.
- Consider rocks which form because of the presence of humans – we can think of these as anthroprogenic.

Rock Cycle


andesite
dacite
rhyolite
basalt
lahar
volcanic tuff
mechanical and chemical weathering
sorting
sediments
gravel, sand, silt, mud, clay
dust
waves
currents
H_2O
mineral precipitation
evaporation
transpiration
peat
gypsum
rock salt
reef buildup
turbidity flows
trophic respiration
deposition
collapse breccia
planktonic ooze
bioaccumulation & bioturbation
lime sediments
disconformity
lignite
soil
colluvium
landsliding
porphyry
lava flows
diabase
nonconformity
serpentinite
hydrothermal veins
granodiorite
intrusive igneous rocks
gabbro
diorite
granite
pegmatite
igneous rocks
pyroxenite
intrusion
crystallization
cooling
plutonism
magma
peridotite
oceanic crust
The Rock
mineralization
uplift
fault breccia
travertine
basalt
earthquake
mylonite
shale
mudstone
siltstone
sandstone
conglomerate
groundwater motion & interactions
compaction cementation lithification
organic maturation
fossilization
gas
oil
bituminous coal
greenstone
chert
metachert
schist
quartzite
metasandstone
metaconglomerate
argillite
subsidence
slate
unconformity
limestone
dolostone
anthracite coal
marble
tectonism
folding & faulting
metamorphism
recrystallization

The Rock Cycle

Volcanic eruptions lead to lava ending up igneous rocks such as pumice and basalt

Rock erosion by the force of water in a river is seen in the Grand Canyon – strata of different rocks are very obvious.

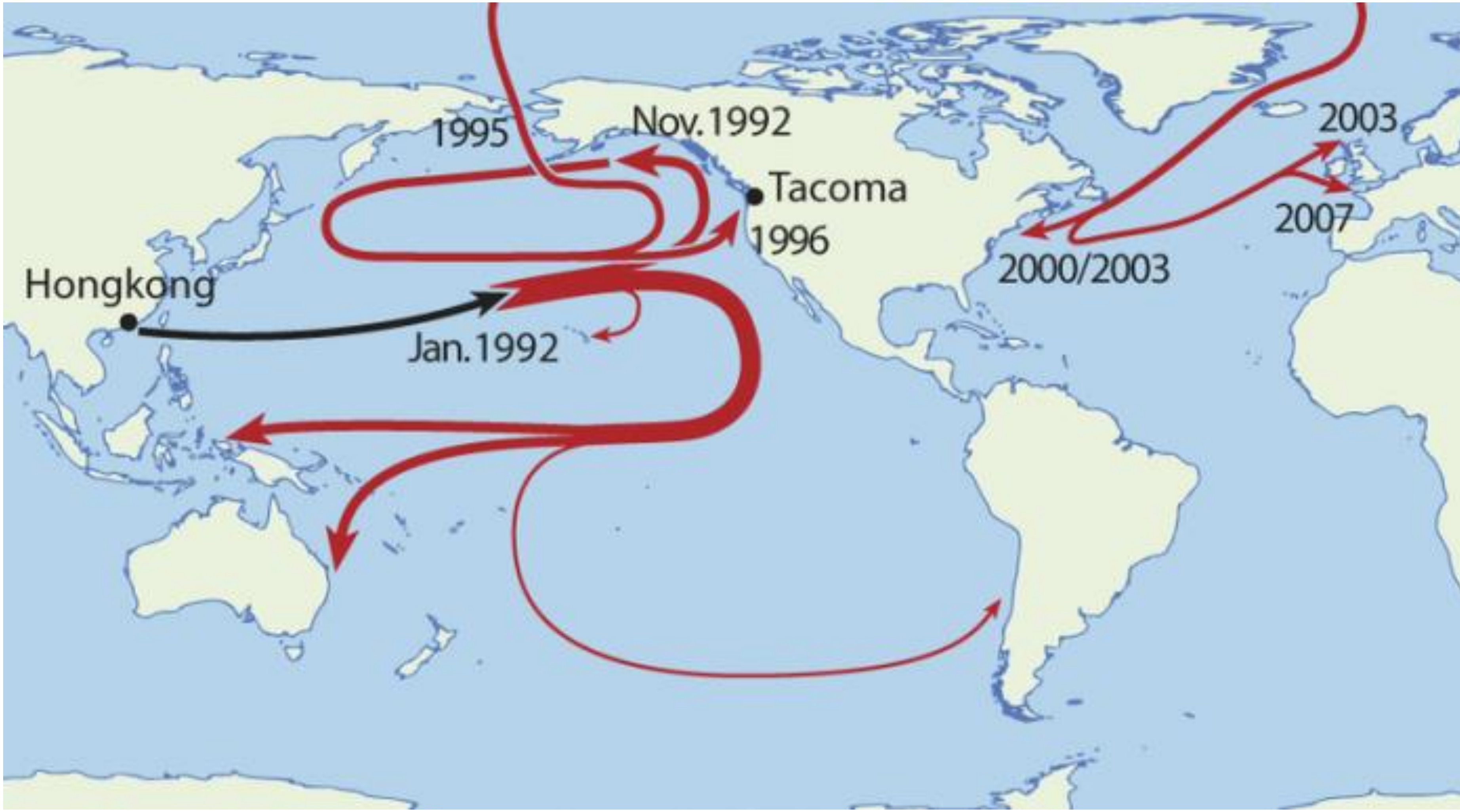
Erosion leads to sediments transported by rivers and settling in the ocean to give sedimentary rocks.

The oceanographic plastic duck(ies)

- In 1992 about 28,000 rubber (synthetic – actually plastic) ducks were plunged into the ocean after a shipping crate was lost at sea on its way to the US from Hong Kong.
- At the time it was put down as a commercial loss and soon forgotten, yet years later these ducks have become famous as a vital tool in our understanding of ocean currents and the distribution of pollutants.
- After being lost overboard in the Pacific Ocean, the ducks made it halfway around the world, washing up on the shores of Hawaii, Alaska, South America, Australia as well as the Pacific Northwest.
- Some ducks were even found frozen in Arctic ice, while other ducks made their way as far as Scotland.
- The ducks are now known as the "Friendly Floatees" by researchers who have tracked their progress over the years.

Friendly floating plastic ducks all at sea

The voyages of the ducks



The fate of Moby Duck

- 2,000 of the ducks circulate the currents of the North Pacific Gyre – a vortex of currents which stretches between Japan, Alaska, Kodiak and the Aleutian Islands – that the plight of the duckies helped to identify.
- Researchers now know that it takes a current three years to circulate the full current by monitoring the ducks' progress.
- Furthermore, the ducks also brought attention to a huge garbage patch which has formed in the North Pacific Gyre, furthering evidence that ocean trash forms in the ocean's gyres. .
- The Friendly Floatees are still washing up to this day and have been the feature of a book chronicling their journey entitled Moby Duck.

The riddle of the rocks

- Since most of this circulating material is not easily degraded it may eventually become part of the rock record, deposited on beaches or in the deep ocean via the digestive processes of fish.
- In fact, North American researchers recently described a new type of solid rock found in Hawaii containing plastic bags, rope and bottle tops…
- They called it plastiglomerate.
- In theory, future generations of geologists could discover discover coloured chunks of plastic embedded within rocks.
- Charles Moore, a sea captain and oceanographer for the Algalita Marine Research Institute in Long Beach California first came across such aggregates whilst surveying Kamilo beach on the Big Island of Hawaii in 2006.

Not just hitting two rocks together, but making new rocks!

- Professor of Geology, Patricia Corcoran and Professor of Visual Arts, Kelly Jazvac of the University of Western Ontario investigated these formations further and coined the name “plastiglomerates”.
- About 20% of the plastiglomerates found on Kamilo Beach contained large amounts of fishing debris, 25% derived from broken lid containers and the rest was mostly constructed of plastic “confetti”, which is the result of the action of the sea in breaking up any solids.
- These combine with natural materials through the action of fire which can be from lava or from campfires.
- The action of the sea within the hydrological cycle is an important way of recylcing elements, but they are not usually so resistant to biodegradtion.

Do huge oceanic vortices mix things up?

- Erik van Sebille of the University of New South Wales in Australia and colleagues confirmed that huge vortices recycling materials exist in the oceans in a study they published in 2012.
- The used a network 20,000 satellite tracked buoys to confirm that there are at least six major patches of plastic garbage in the oceans.
- Five of the ones they found are in the subtropical seas and the sixth is in the Barents Sea in the Arctic.
- The bad news is that plastic migrates between these patches, so even if nearly everyone stops polluting the seas with plastic, it only takes on bad neighbour to perpetuate the problem.
- And the timescale if everyone behaves?
- Not known – a truly man-made problem.
- And the shocking part is that van Sebille estimates that in the North Pacific there is probably more weight in plastic than there is in life forms.

Man makes his mark

Since plastiglomerates, like these, are likely to stay in the rock record, they may serve as another global marker for the Anthropocene, a possibly new geological era marking the time period when humans significantly altered Earth's physical, chemical and biological landscape.

A clastic anthropocene rock

Inclusion of fishing gear into rocks

These are large parts of the tiny pieces of plastic found throughout the biosphere

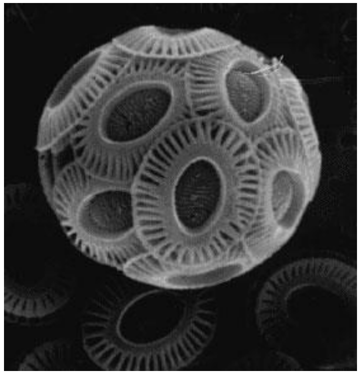
Small plastic fragments, shown here, are a huge problem on Hawaii's beaches. At Kamilo Point on the Big Island of Hawaii, where this photo was taken, such fragments may penetrate 3 feet down in the sand.

BUT humans were not the first organisms to fiddle with geology!

Calcium biominerals provide another take on life interacting with geology to give new rocks.

Examples include many calcium carbonate and calcium phosphate Minerals, usually as hybrid materials

A few well known examples of calcium containing biominerals




Biomineralisation & Crystal Tectonics

- **Biomineralisation**

The study of the formation, structure and properties of inorganic solids deposited in biological systems.

Crystal formation by organisms is commonly controlled by extracellular proteins and polysaccharides.

- **Crystal Tectonics**

Assembly of individual biomineral crystals into more complex structures such as shells or spines.

Biomineralisation as an Inspiration to Synthetic Chemists

Reproducing the structures formed through biomineralisation is the best way to gain insights into the natural processes.

Synthetic structures could find uses in areas such as bone replacement therapy, sensing, ultra light and strong materials etc.

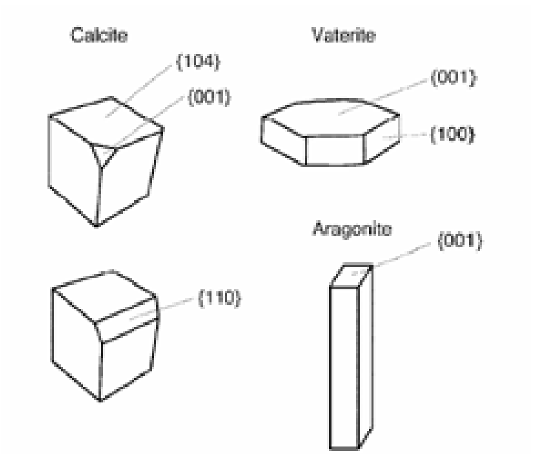
Overall the study of biomineralisation provides a platform for chemists to learn how to control in a tailored fashion the properties and functions of material structures.

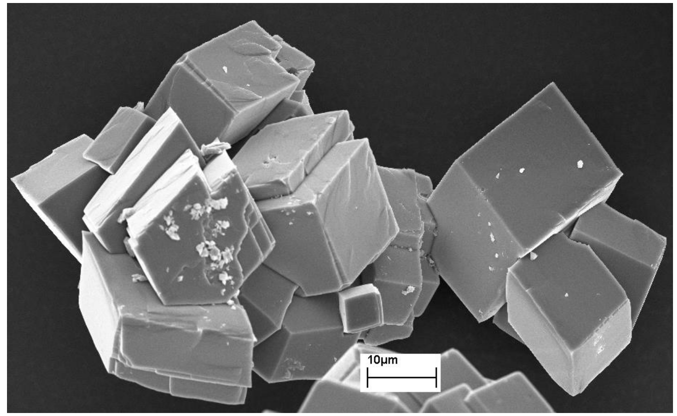
Carbon balance through biomineralistion

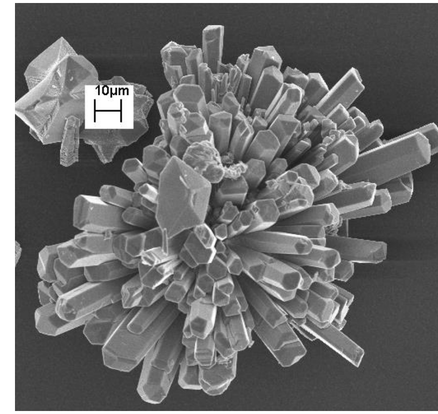
$CaCl_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2NaCl + CO_2$

- The pH of seawater and its ionic strength favour the formation of calcium carbonate minerals by aquatic creatures.
- If these conditions are changed, there is the danger that on formation of one mole of carbonate (fixed CO_2) one molecule of CO_2 will also be released instead of redissolved into the aquatic medium.
- Much of this carbon fixation (uptake of bicarbonate) is achieved by carbonic anhydrase pathways – this is especially important for corals.
- Organisms are able to steer the calcium minerals (here carbonates) in order to fulfil specific functions – hard spines, soft insides to shells, etc.
- For seawater creatures the easiest mineral to produce is to combine dissolve CO_2 in the form of bicarbonate with Ca(II) to give one of the three crystalline polymorphs of $CaCO_3$ or else its amorphous form.

Polymorphs of calcium carbonate

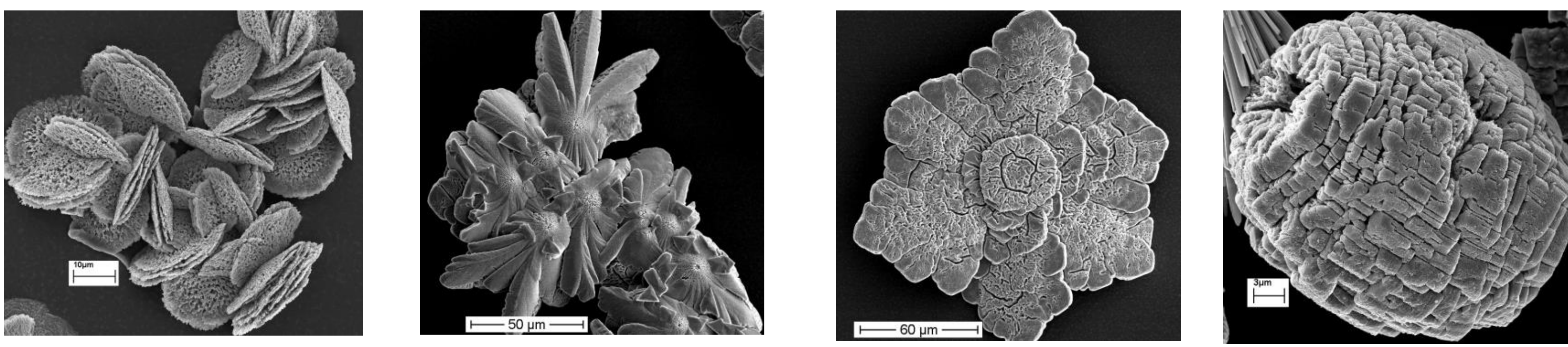






Calcite

Aragonite



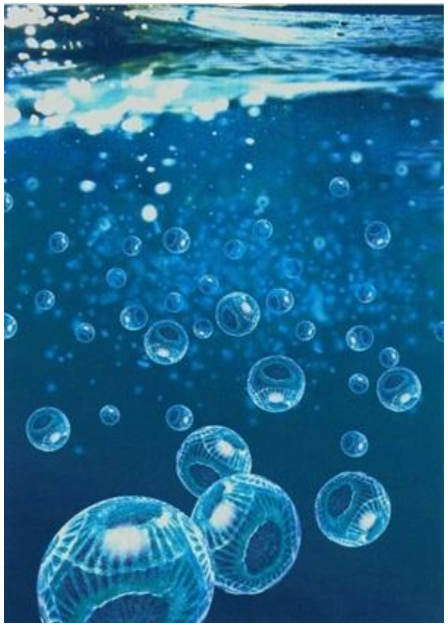
Vaterite

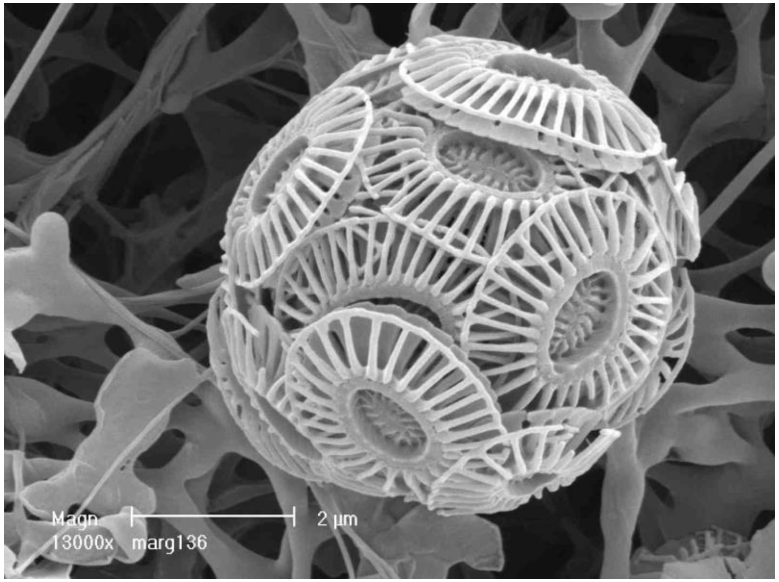
Calcium carbonate biominerals

Mineral	Formula	Organism	Location	Function
Calcite	$CaCO_3$	Coccolithophores Molluscs Crustaceans Birds Mammals	Cell wall scales Shell Crab cuticle Egg shells Inner ear	Exoskeleton Exoskeleton Mech. strength Protection Gravity sensor
Aragonite	$CaCO_3$	Molluscs Fish	Shell Head	Exoskeleton Gravity receptor
Vaterite	$CaCO_3$	Gastropods Acidians	Shell Spicules	Exoskeleton Protection
Amorphous	$CaCO_3 . nH_2O$	Crustaceans Plants	Crab cuticle Leaves	Mech. strength Calcium store

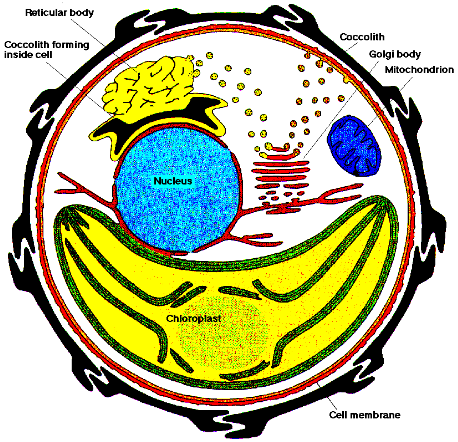
Algal Bloom

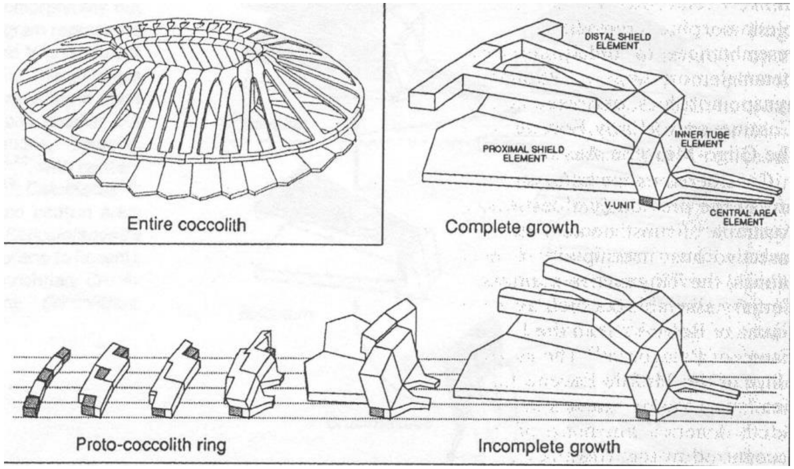
Coccolithophores: the most famous example, E. Huxleyi



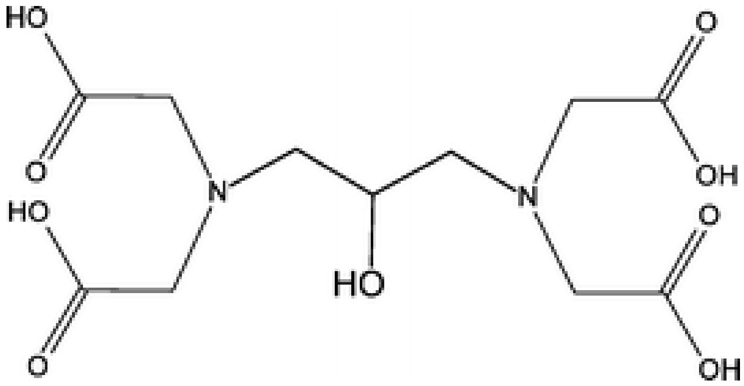


Coccosphere of **Emiliania Huxleyi**





Biomimetic assembly of calcite microtrumpets



As often found in natural biomineralisation, the ligand plays a role in dictating the structure, but we do not see where it is in the end product.

1,3-diamino-2-hydroxypropane-*N,N′,N′,N′* -tetraacetic acid (H_5hpdta)

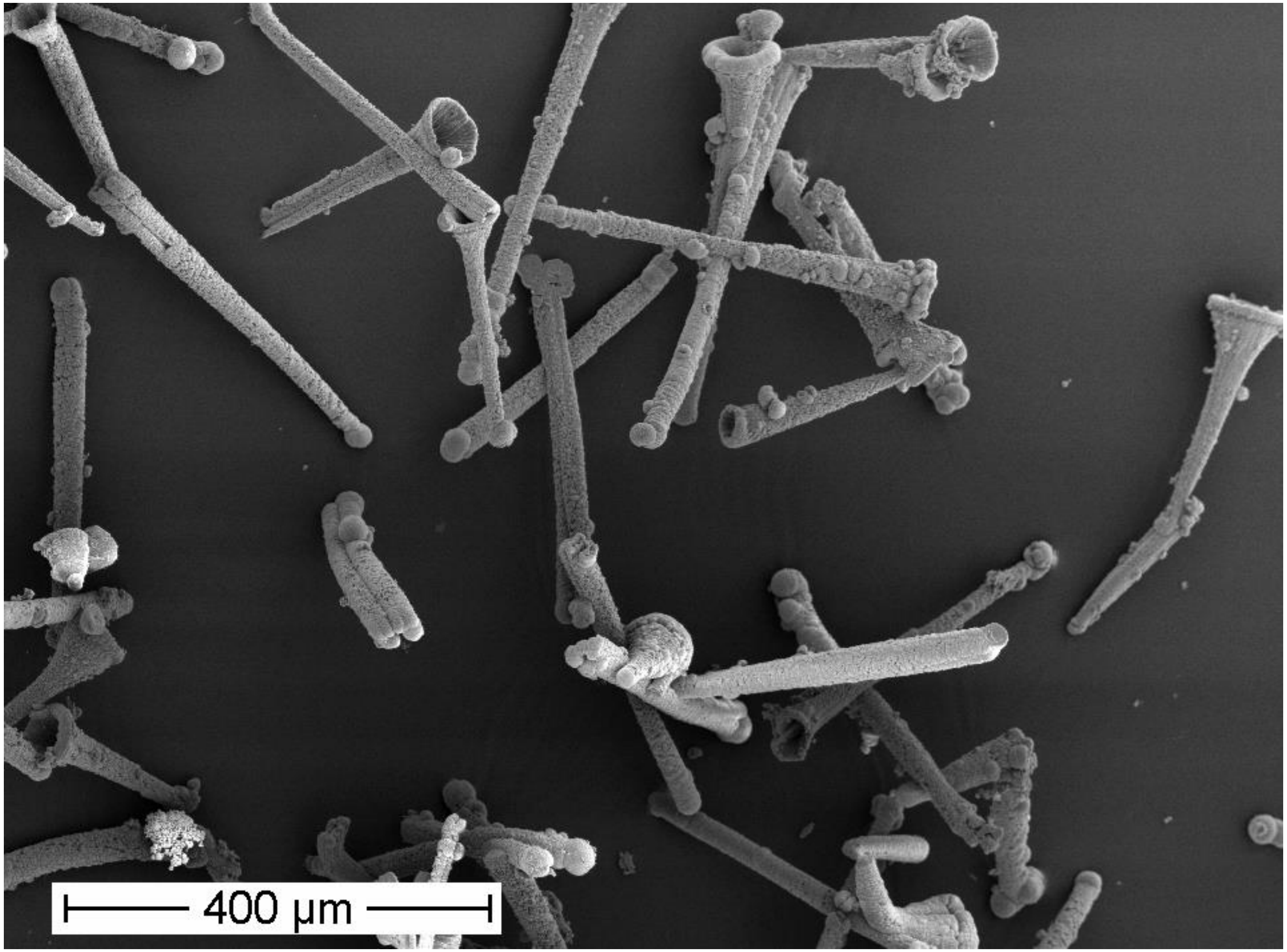
When this polycarboxylate is present the mineralisation of calcium carbonate is modified to give calcite microtrumpets!

$$CaCl_2 + 2NaHCO_3 + x\ H_5hpdta \rightarrow CaCO_3 + 2NaCl + CO_2$$

Where is the H_5hpdta?

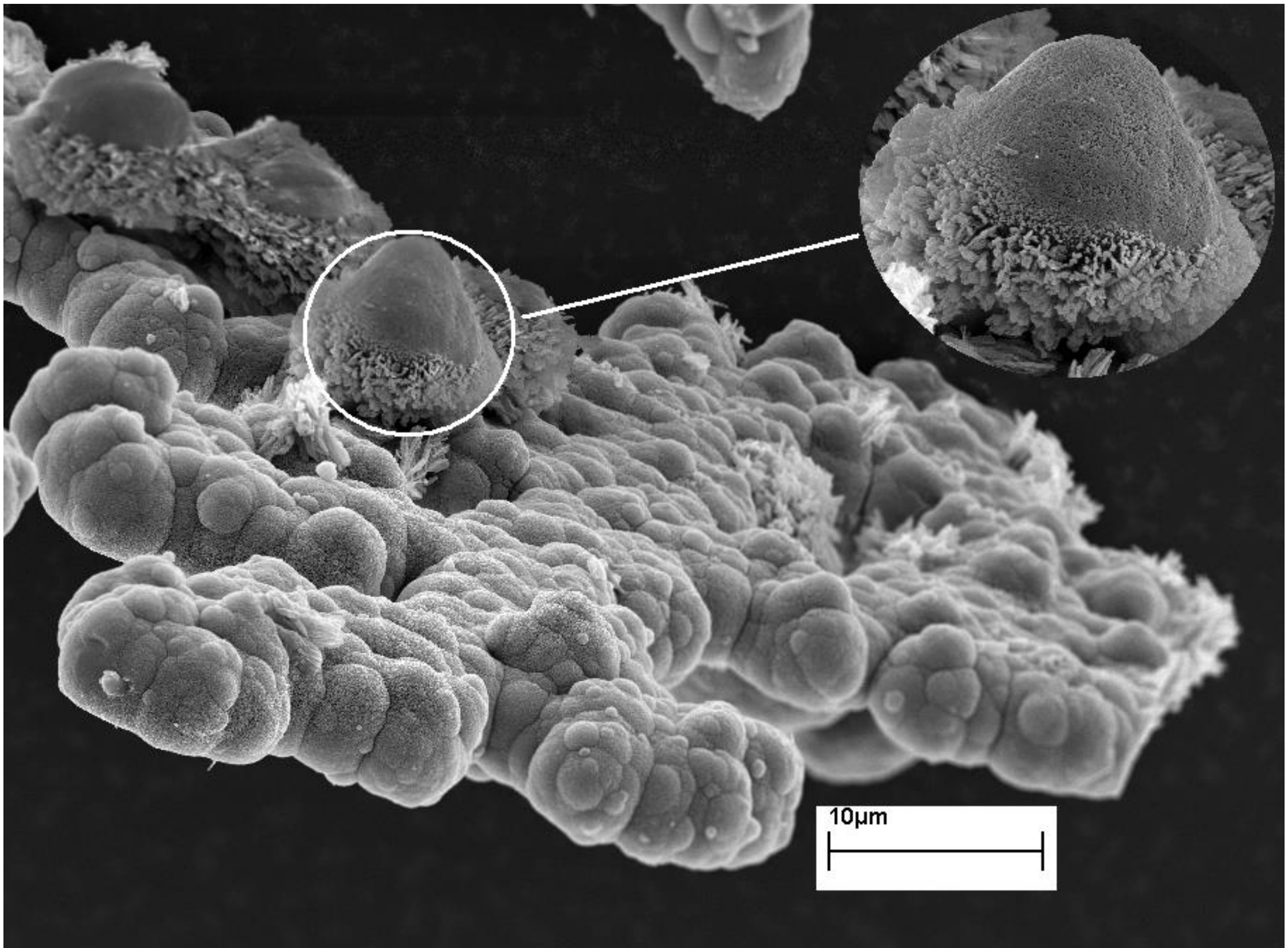
Sarat B. Mukkamala, AKP, Chem. Comm., 2005

Biomimetic assembly of calcite microtrumpets



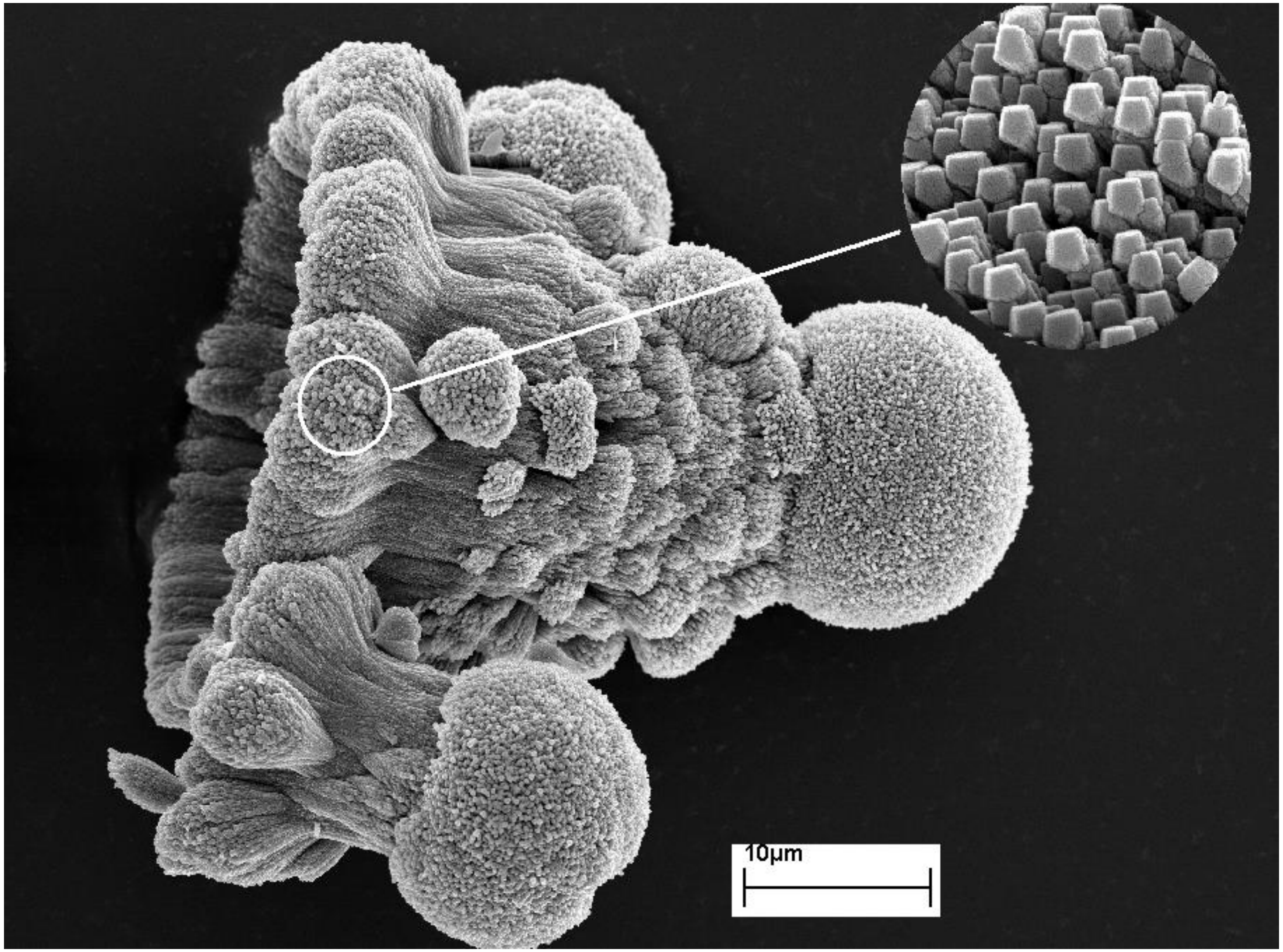
Biomimetic assembly of calcite microtrumpets

SEM of calcite formation after 6 h



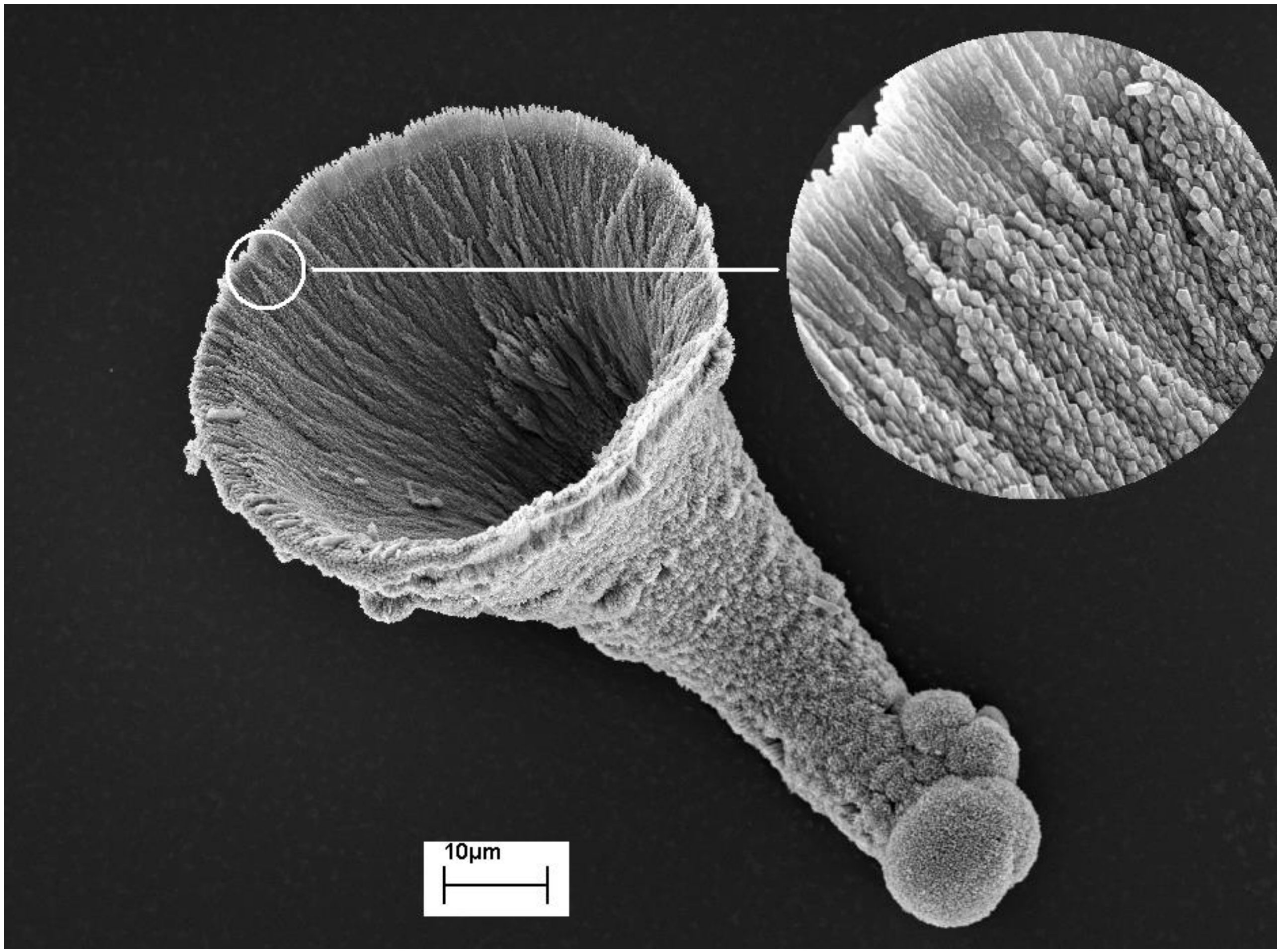
Biomimetic assembly of calcite microtrumpets

SEM of calcite formation after 12 h

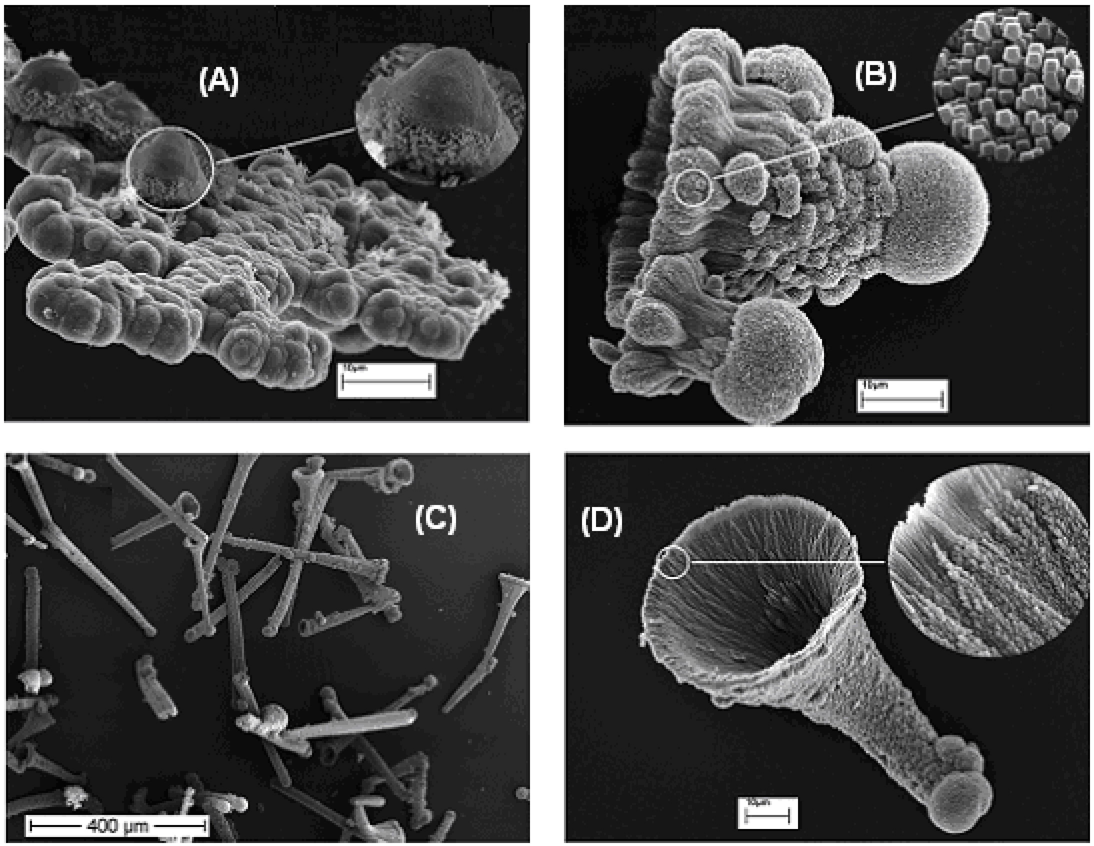


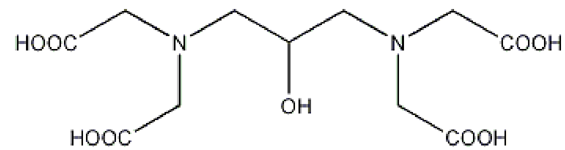
Biomimetic assembly of calcite microtrumpets

SEM of calcite formation after 24 h

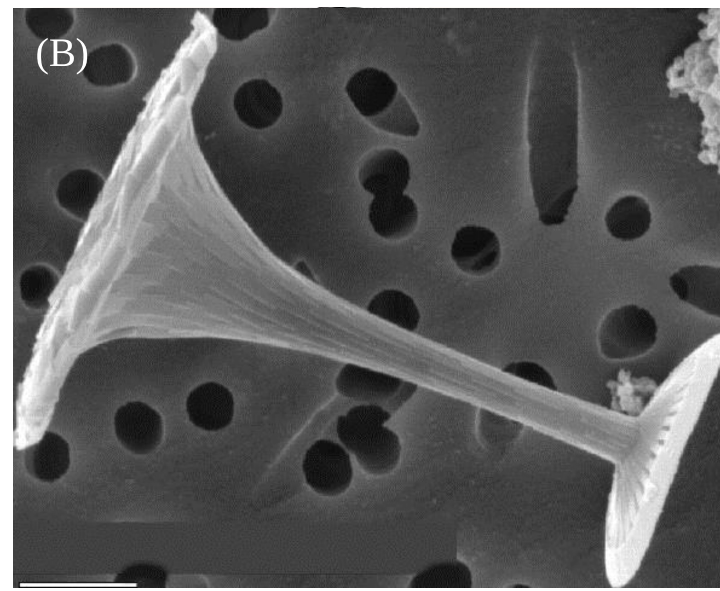


Summary of the $CaCO_3$-Trumpets





1,3-diamino-2-hydroxypropane-*N*,*N*,*N′*,*N′*-tetraacetic acid (H_5hpdta)



Discosphaera Tubifera

So what next?

- Humans have to try to discover a useful context for their existence on Earth – this isn’t easy given their extremely rapid development and consciousness of their surroundings and sense of responsibility,- never mind how misplaced that might be.
- The speed of change wrought on the Earth by human activities is potentially beyond what the adjustment of the dynamic equilibria which keep the planet in its Goldilocks state can cope with.
- The growth of the human population is also an issue.
- Let’s ask ourselves if we can do better than than the cyanobacteria!
- We have all the emotional equipment to do something about all of this – it just takes some concerted effort.
- The alternative it is to leave the Earth and leave it to do things its way…

aug 9

Drop in ocean pH levels spurs talks

STAFF REPORTER

ideas th

Up to 45 international e
Commonwealth marine
science officials will gat
University of Otago next
discuss the fight against
acidification.

Acidificat
workshop
February 17 to 19, is the
undertaken by the high-l

Dr Christina McGraw,
University of Otago's De
Chemistry, and chairwo

Community
in pH of our
acidificat
influence

something that is happe

"We can't stop it until
carbon emissions, but w
thinking about ways to p
mitigate for it.

I despair at the lack of climate urgency

Mike Jo

B

What Mike Joy, senior researcher at Victoria University, Wellington, despairs about in "Opinion", The Press) 20/03/19

- … I'm inundated by revelations of the accelerating dissolution of our planet's life-supporting capacity…
- …Despite the warning signs, all I see around me is business as usual, with economic growth still the supreme imperative…
- …Since I was a child we have wiped out 60 per cent of animal populations; the current extinction rate is 1000 times higher than background rates…
- …in the early 1990s came the World Scientists' Warning to Humanity, and last year a more urgent "Second Warning to Humanity… Both warnings unambiguously declared that if we don't change the way we live, the planet will soon no longer support us…

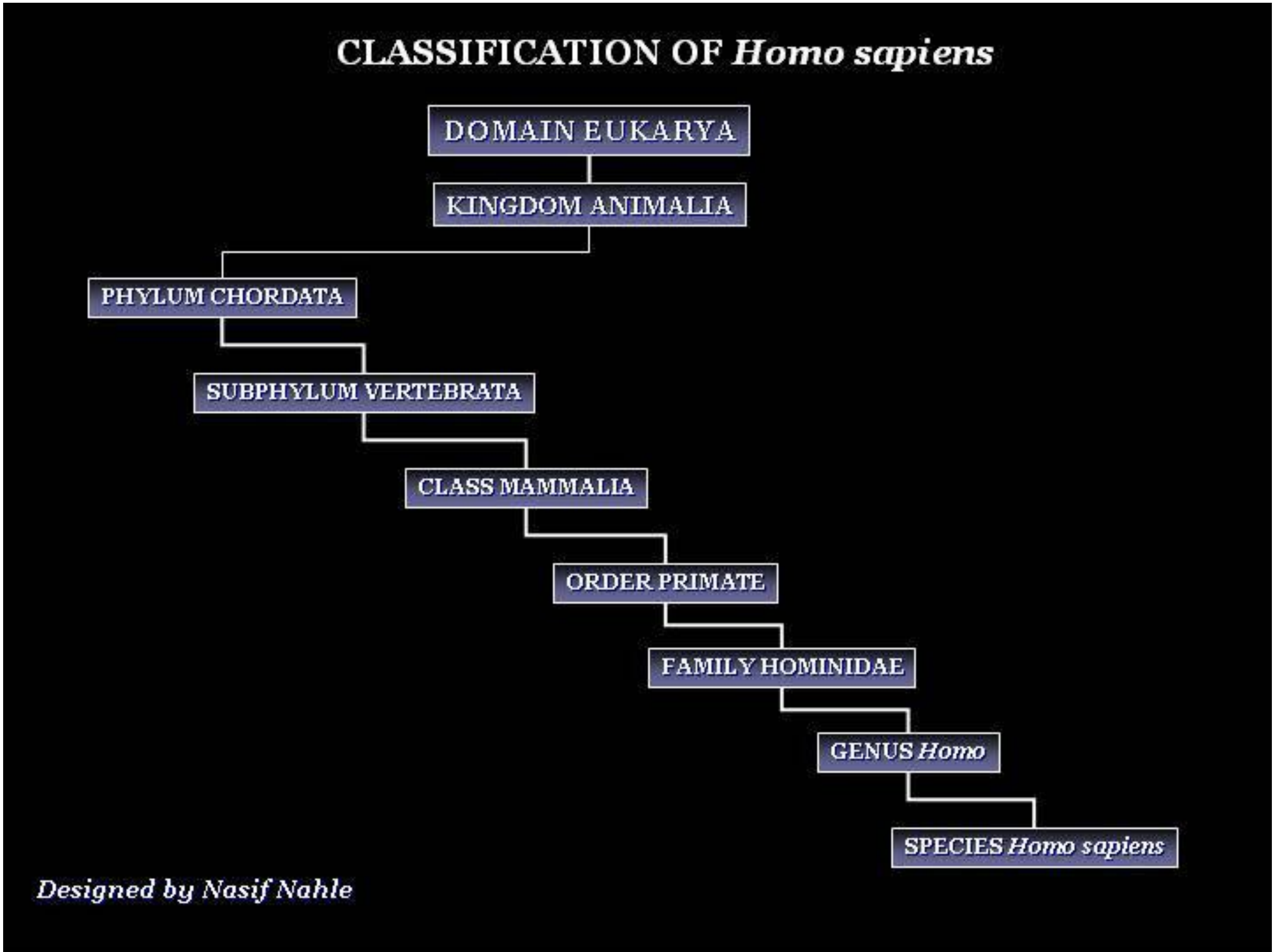
Mike Joy continues…

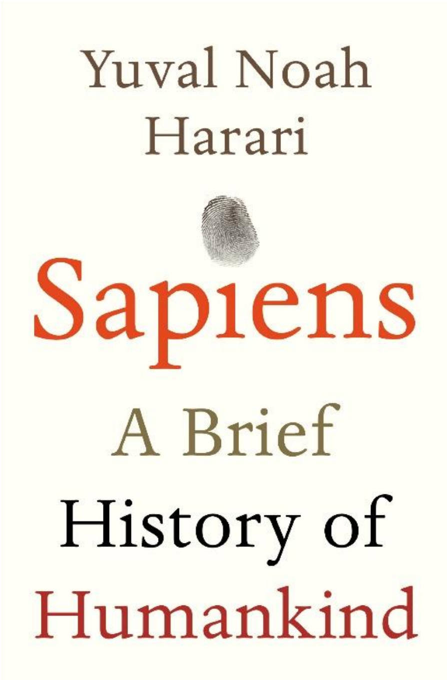
- …renewable energy has not replaced any other form of energy. It has only been added to the mix. We now use proportionally more fossil energy than at any other time in history.
- …The fact is that the world economy remains hopelessly coupled to fossil fuel.
- …We need to reduce greenhouse gas emissions by 6 per cent a year from now until 2050 to have a hope.
- …GDP is inextricably locked to greenhouse gas emissions so achieving that reduction would require ongoing reductions in GDP.
- …I hope that in my role as a scientist I can help raise the necessary public awareness
- …It’s time we all woke up. The house is on fire. If we don’t put it out, our children are going to burn.

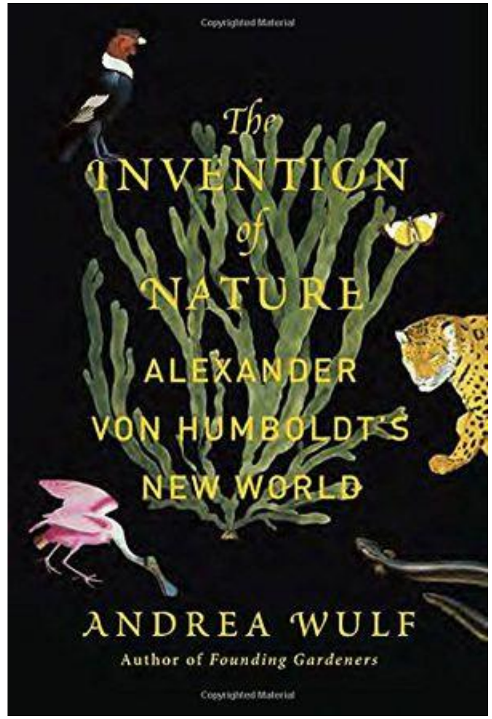
New date for Mt Taranaki's last big blast

eruptions
500 year
about 90

We wonder whether we are alone in the Universe when we have made ourselves alone at home!




Yuval Noah
Harari
Sapiens
A Brief
History of
Humankind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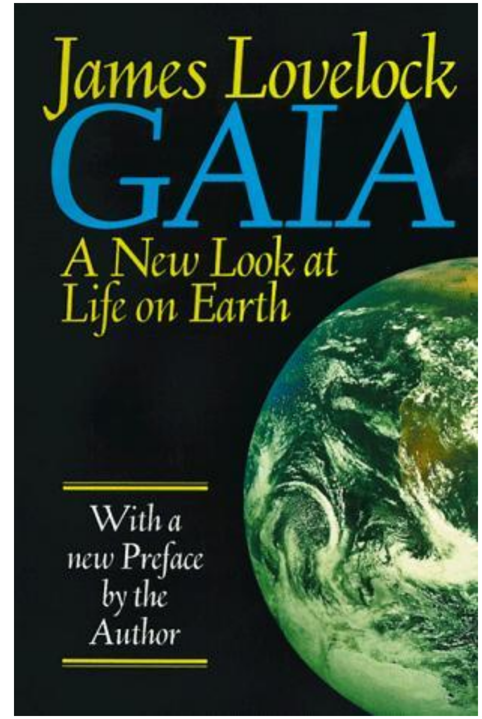
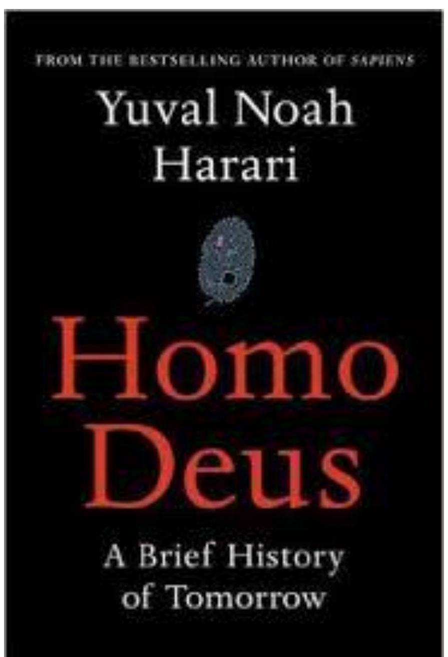
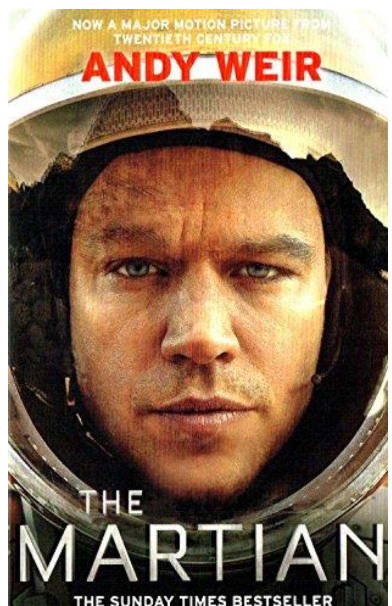
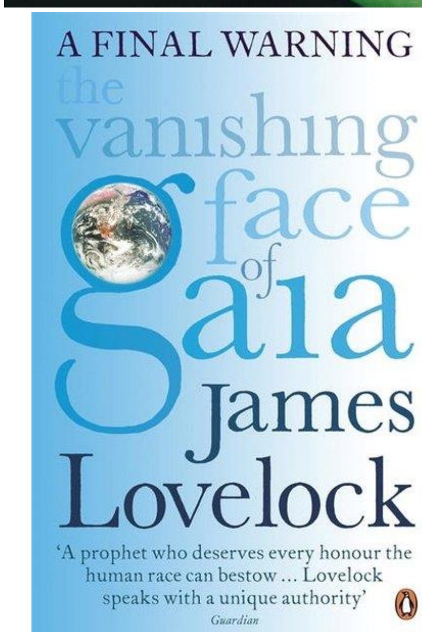

James Lovelock
GAIA
A New Look at
Life on Earth
With a
new Preface
by the
Author


FROM THE BESTSELLING AUTHOR OF SAPIENS
Yuval Noah
Harari
Homo
Deus
A Brief History
of Tomorrow


ANDY WEIR
THE
MARTIAN
THE SUNDAY TIMES BESTSELLER


A FINAL WARNING
the
vanishing
face
of
gaia
James
Lovelock
'A prophet who deserves every honour the
human race can bestow ... Lovelock
speaks with a unique authority'
Guardian

Colonise Mars…?

What does the fairy story of Goldilocks tell us?

Mars (too cold)   Earth (just right)   Venus (too hot)

Not too hot, not too cold, but "Just right!" as Goldilocks said about the Little Bear's porridge (and that was all eaten up – oops!)

Which all goes to show that, actually,
women are from Mars and men are from Venus
– as if we didn't know!

The alternative Goldilocks Story…

Concluding Remarks

- Of course – we are not separate from the "rest" of biology – but we do understand the consequences of what we are doing.
- Note that "innocent" biology has been responsible or may become so for several near environmental catastrophes.
- In the meantime, mankind has made such fast progress on agricultural, industrial and increasingly on aquacultural levels that the response of the Earth may be to go into catastrophic change, possibly in order to regain a "friendly" state for future attempts at life/Earth interfacing (see "The Gaia Principle by James Lovelock and also the writings of Alexander von Humboldt).
- Probably the most important gases to keep under control at the local level are oxygen, nitrogen, carbon dioxide, methane and water vapour.
- BUT, we also need to maintain watch over other low concentration gases such as nitrogen and sulfur oxides as well as gaseous DMS and DMSO.