

U3A Geology Group

Summary – Session 4

The Evolution of the Atmosphere

Sources of Evidence

Present composition of....

- ...the Earth's atmosphere
- ...the atmospheres of other planets
- ...the Sun
- ...gases trapped in meteorites
- ...gases emitted by volcanic activity

Compositions may be described in terms of....

-**chemical** make-up
-**isotopic** make-up.

In this discussion, only covering **chemical** make-up, but **isotopic** evidence has been of equal importance.

Present composition of Earth's atmosphere

	Nitrogen	78.08%		
	Oxygen	20.94%		
	Argon	0.93%		
	Carbon dioxide	0.038%		
	<i>Noble gases</i>		<i>Some other components</i>	
Neon	0.0018%		Methane	0.00017%
Helium	0.00052%		Hydrogen	0.00005%
Krypton	0.000114%		Dinitrogen monoxide	0.00003%
Xenon	0.0000086%			

Water vapour - variable (0 - 0.7% at 15 °C at sea-level)

Variable trace amounts: hydrogen sulphide, sulphur oxides, carbon monoxide, ammonia

HYPOTHESIS 1

Earth was born with an atmosphere collected from the gases of the original nebula, and that simply evolved to its present composition.

If so, there should be similarities with the atmospheres of some of the other planets in the solar system.

Outer planets – the gas giants:

Jupiter

hydrogen	89.8±2.0%
helium	10.2±2.0%
methane	0.3%
ammonia	0.026%
hydrogen deuteride	0.003%
ethane	0.0006%
water	0.0004%

Saturn

hydrogen	96%
helium	3%
methane	0.4%
ammonia	0.01%
hydrogen deuteride	0.01%
ethane	0.0007%

The atmospheres of these planets are closely similar to each other and contain as main components:

hydrogen helium methane
ammonia noble gases

- probably reflect the gas composition in the nebula from which the solar system formed
- contain krypton and xenon in significantly higher proportions than Earth's atmosphere

These atmospheres are considered to be **primary atmospheres** formed when the planet itself was formed.

Inner planets: Mercury to Mars

	Mercury	Venus	Earth	Mars
carbon dioxide	0	96.5%	0.038%	95.32%
nitrogen	0	3.5%	78.08%	2.7%
carbon monoxide	0	0.0017%	trace	0.07%
sulphur dioxide	0	0.015%	trace	trace
argon	0	0.007%	0.93%	1.6%
helium	0	0.0012%	0.00052%	0
neon	0	0.0007%	0.0018%	0.0000025%
<i>Surface pressure</i>	0	92 bars	1 bar	0.00075 bar
<i>Average temperature</i>	-168°C to 427°C	464°C	15°C	- 125°C to - 225°C

From this evidence:

- The atmospheres of these planets are so different from each other and from the primary atmospheres of the gas giants that they must represent atmospheres created by events occurring later than the formation of the planets themselves.
- Such atmospheres are said to be *secondary atmospheres*
- *Conclusion:* if Earth ever had a primary atmosphere, it may have been similar to that of the gas giants, but that must have been altered beyond recognition by later events, or even escaped entirely

So we have to abandon our first hypothesis!

HYPOTHESIS 2:

Earth's atmosphere has come from gases given out from within the planet during its lifetime - *out-gassing*.

Evidence:

Present-day emissions of volcanic gases...

- produce all the components found in the present atmosphere except free oxygen
 - also produce some of the components of the present oceans
 - probably result from the same out-gassing processes that occurred during and ever since the formation of the Earth, though at a diminishing rate.
1. We can account for the differences in composition between volcanic emissions and the present atmosphere by other known processes.
 2. If all the inner planets formed atmospheres by out-gassing, the differences between their present atmospheres can be accounted for by different processes under different conditions – *each planet has a different chemical history!*

We have no better hypothesis at present!

From volcanic gases to our atmosphere?

Composition of Atmosphere

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methane	0.00017%
krypton	0.000114%
hydrogen	0.00005%
dinitrogen monoxide	0.00003%
xenon	0.0000086%
water vapour	variable <0.7%
hydrogen sulphide, sulphur oxides, carbon monoxide, ammonia	variable traces

Volcanic Gases - Hawaii

nitrogen	4.7%
oxygen	0
argon	0.2%
carbon dioxide	11.8%
water vapour	73.5%
sulphur oxides	8.9%
hydrogen	0.4%
others	0.5%

So we will need some good ideas to explain the differences! Let's take the major gases one at a time...

OXYGEN

Hypothesis:

The presence of oxygen in our present atmosphere might be accounted for by chemical processes only.

By analogy with volcanic gases, the original out-gassed atmosphere could have contained...

...mainly

carbon dioxide ~80%

nitrogen ~20%

water vapour (now in the oceans!)

...minor amounts of

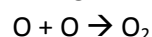
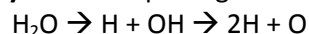
ammonia methane

hydrogen other reducing gases

noble gases – especially argon

So how could oxygen have been produced by a simple chemical reaction?

1. Solar ultraviolet radiation on the **early** Earth → splitting of water molecules (photo-dissociation)



to create tiny amounts of free oxygen (*this process still occurs in the upper atmosphere today*)

The **maximum** concentration of oxygen that could have existed as a result of this process in the early atmosphere has been calculated (in terms of its partial pressure) to be about

$$5 \times 10^{-9} \text{ bar}$$

i.e. 5 billionths of a bar - miniscule, but not zero! (*Compare present partial pressure of oxygen at 0.2 bar*)

2. Sedimentary rocks older than ~2.5 Ga contain minerals that react readily with oxygen. (e.g. pyrite, FeS₂; uraninite, U₃O₈)

This is calculated to set an **upper** limit on the partial pressure of free oxygen at:

$$2 \times 10^{-4} \text{ bar}$$

The same rocks also contain magnetite, Fe₃O₄, which requires the presence of free oxygen. This is calculated to set a **lower** limit on the partial pressure of free oxygen at

$$\sim 10^{-11} \text{ bar}$$

3. The combination of ...
...photo-dissociation producing oxygen and
...minerals (pyrite and uraninite) removing oxygen
probably did balance to produce a tiny but persistent concentration of oxygen in the early atmosphere.

BUT these chemical processes could never have made oxygen into a major component of our atmosphere!

Hypothesis:

The proportion of oxygen in the present atmosphere is the result of biological processes

So is there evidence for a link between evolution of life forms, and of the oxygen content of the atmosphere?

Classification of Living Organisms

All living organisms can be classified by their basic cell structure into two major types:

prokaryotes and eukaryotes

Prokaryotes:

- are all single-celled organisms, but may form colonies
- have no nucleus – genetic material is not separated from rest of the cell
- form two distinct, unrelated **domains**:

archaea and bacteria

both sub-divided into many phyla.

Eukarya form the third domain of life, and:

- may be single-celled, but include all multi-cellular organisms
- have a cell nucleus containing their genetic material
- divide into three **kingdoms**:

moulds & fungi

plants

animals

Archaea

- characteristic biochemistry – distinct from bacteria
- fossils date from before 3.5 Ga
- can live in a remarkable range of environments, including hot springs and black smokers
- derive energy from a range of chemical reactions which are NOT based on oxygen

Bacteria

- the most varied and prolific group of organisms on the planet (but archaea are not far behind in numbers!)
- can also live in a remarkable range of environments, including hot springs and black smokers where many derive energy from a range of chemical reactions which are NOT based on oxygen
- include the cyanobacteria (*previously known as blue-green algae*) whose ancestors were the first organisms to evolve the process of **photosynthesis** about 3.3 Ga
- so probably were responsible for increasing the amount of free oxygen from that time.
- also responsible for transferring carbon from CO₂ in the atmosphere to carbon in sea-floor sediments, and not just as a result of photosynthesis

Photosynthesis

Basic process: **carbon dioxide + water → glucose + oxygen**

But this process goes 'uphill' in energy terms, so requires an input of energy (it is **endothermic**).

The energy is supplied as visible light, using wavelengths (colours) in the red and blue regions of the spectrum.

(Which is why leaves are green – unused part of the spectrum is reflected).

The process requires a complex series of reactions enabled by a catalyst – **chlorophyll**.

Bacteria and Early Photosynthesis

- All prokaryotes lack a nucleus, so their DNA is 'unpacked'.
- DNA is particularly vulnerable to damage from ultra-violet radiation from the Sun.
- Little or no oxygen in the atmosphere when photosynthesis began, so no protective ozone layer.
- Photosynthesis possibly began by extracting hydrogen atoms from hydrogen sulphide, H₂S, rather than from water, H₂O
- So ancestors of cyanobacteria must have had another strategy to avoid UV damage.
- Modern photosynthesising bacteria in the oceans (phytoplankton) shut down their photosynthesis in the middle of the day to avoid damage.
- Ancestors of cyanobacteria probably lived about 10 m below the ocean surface as a protective strategy – enough depth of water to absorb sufficient UV.
- This suggests a scenario in which bacterial and archaean life proliferated in the oceans ~3.5 Ga, and a photosynthesising species of cyanobacteria evolved in a favourable part of this environment
- e.g. near black smoker vents in shallow water?

The Story So Far

- earliest atmosphere of carbon dioxide and nitrogen
- photo-dissociation by UV in upper atmosphere forms tiny amounts of oxygen
- balance between such oxygen production and oxygen removal by reducing minerals
- earliest living organisms, probably cyanobacteria, evolve capacity to photosynthesise in the upper layers of the oceans about 3 – 3.5 Ga
- but reducing minerals continue to keep oxygen levels in the atmosphere at low levels, though carbon dioxide levels go down
- some time in the next billion years, cyanobacteria evolved to produce oxygen from water by photosynthesis

so how long did this removal of oxygen continue?

- less than 5% of Earth's surface was land until 2.5 Ga – 95%+ ocean!
- evidence from 2.6 Ga rocks in South Africa that bacteria may have colonised the land at this very early stage
- but if they did, there must have been a protective ozone shield, which implies an oxygen-rich atmosphere!
- so we still need more evidence for the rate of increase in oxygen levels 3 - 2.Ga.
- and what was happening to carbon dioxide levels?

Eukarya

- have cells with a nucleus
- need a partial pressure of oxygen > 10⁻³ bar to function
- appear as fossils about 2 Ga

Soft-bodied metazoan animals *e.g. jellyfish*

- absorb dissolved oxygen from water through outer surface
- require a partial pressure of oxygen > 0.02 bar for this
- appear in the fossil record about 0.6 Ga

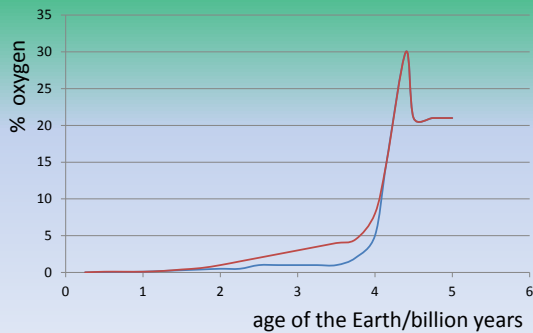
Land Plants

- appeared as fossils about 0.45 Ga (may even have preceded land plants)
- have already captured photosynthesising bacteria and incorporate them into their own cells as **chloroplasts**
- spread abundantly as Coal Measures forests about 0.3 Ga
- were involved in widespread forest fires at this time

Land animals

- appeared as fossils about 0.3 Ga
- require oxygen levels around present value - ~0.2 bar

Oxygen levels over time



Summing all this in a graph...

It is estimated that **algae** today produce about 73 to 87 percent of the net global production of oxygen.

Why the Delay?

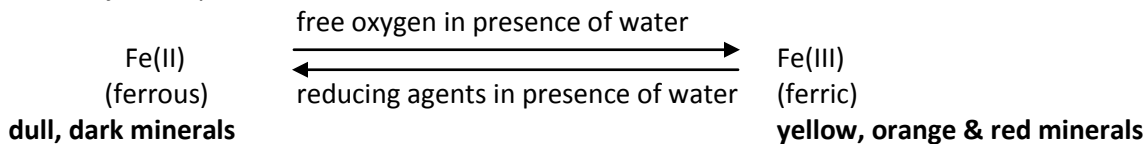
- If photosynthesis evolved around 3 Ga, why did it take so long to get to its present level?
- Why the dramatic increase to present levels in less than 0.5 billion years?
- What's the evidence to explain these?

Evidence from Fossil Record and Biology

1. No ozone layer > restrictions on habitat - oceans
2. Archaea and bacteria as only common life forms
3. Protective ozone shield probably required 0.5% oxygen

Evidence from the Rock Record

- certain elements can act as 'oxygen indicators' in rocks
- especially minerals containing iron, sulphur and uranium, which are easily oxidised or reduced according to conditions
- iron is a major component of most rocks!



- so igneous rocks with Fe(II) minerals → dark colours
- black smokers produced large amounts of Fe(II) which dissolved on the anoxic ocean water and which reacted with carbonate ions (CO_3^{2-}) from algal limestones to form **DARK** insoluble oxides and hydroxides of iron
- then when carbonate supply declined, silica gel precipitates and fine shale sediments hardened into layers of chert, often **RED**.
- Result: **banded iron formations (BIFs)** found on ancient continental cratons worldwide, common 2.75-1.9 Ga
- probably represent the continued removal of steadily increasing amounts of oxygen dissolved in the oceans from increasing numbers of cyanobacteria
- include the time of the **Great Oxidation Event, 2.4 Ga** (or the Oxygen Catastrophe!)
- before the GOE: free oxygen effectively all ended up in the BIFs until these sinks were saturated.
- after the GOE: chemical sinks unable to capture all the photosynthetic oxygen produced, so accumulated in the atmosphere.
- oxygen is poisonous! Probably wiped out most of Earth's anaerobic inhabitants – a very significant extinction event
- when these rocks weather in presence of oxygen → yellow/red sediments with Fe(III) → **red beds**
- **red beds** are first found around 2.2 billion years BP, and become increasingly common after that.
- but until most of the Fe(II) involved in the rock cycle had been oxidised to Fe(III), slow build-up of oxygen
- this is assumed to have happened by 0.6 Ga

But what about carbon dioxide?

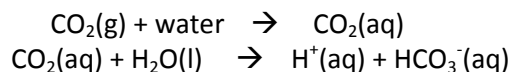
From up to 80% of the original atmosphere...

Two possible sinks: *photosynthesis*

...to 0.038% of the present atmosphere!

solution in sea-water ...and these are inter-related.

Removing carbon dioxide



$\text{HCO}_3^-(\text{aq})$ (bicarbonate ions) can be removed from the sea-water by:

- forming insoluble carbonates, e.g. CaCO_3 (calcium carbonate), by precipitation OR organisms forming shells
- photosynthesis by aquatic organisms such as cyanobacteria, algae (seaweed), plants, etc., to form organic compounds. After death these may oxidise back to CO_2 , or form organic deposits (eventually coal and oil).

With no or little free oxygen there could be no aerobic decay processes oxidising organic matter back to carbon dioxide after death. so dead organic detritus would

either accumulate in sea-floor sediments (Archaean rocks contain ~0.1% carbon)

or be used as food by methanogen bacteria, generating 0.25% methane level in atmosphere

Whether by direct precipitation, or by accumulation of shell material after death, calcium carbonate will eventually end up as sediment on the sea-floor, in course of time turning to **limestone** rock.

Carbonate rocks such as limestones are known from about	3 billion years BP
fairly common from about	2 billion years BP
increasingly abundant from	0.6 billion years BP

All this suggests that biochemical processes are more important than inorganic chemical processes in removing carbon dioxide from the atmosphere.

Net result

- a decrease in CO₂ level, rapidly from 3.5 Ga until 2 Ga
- a rapid decrease as photosynthesis produced a rapid increase in oxygen level
- a further drop of 45% about 0.4 Ga as land plants evolved very rapidly

Today, phytoplankton are calculated to deposit the equivalent of 16 billion tonnes of organic carbon on the ocean floor each year.

Evolving Minerals!

- Recently recognised (November 2008) that the range of minerals in Earth's rocks has evolved in line with the evolution of life and the atmosphere!
- Pre-solar nebula ~ 12 minerals in dust grains of the nebula
- Sun powers up → ~60 minerals
- Planetary formation → ~500 minerals
- Plate tectonics starts → ~1500 minerals
- Life begins ~3.5 - 4 Ga → steady increase to ~5000 minerals
- Oxygen in atmosphere responsible for about half of these
- Carbon removal in the minerals in carbonate rocks, coal, oil are all linked to evolution of life

Nitrogen and argon

- in present atmosphere, nitrogen at 78% and argon at 0.93% → proportion N:Ar of **80:1**
- in average volcanic gas emissions, nitrogen at 4.7% and argon at 0.2% → proportion N:Ar of **23:1**
- both gases are chemically unreactive, so we need an explanation of this big difference!
- nitrogen used in life processes to form proteins should mean a *lower* proportion of nitrogen
- so, why is there so much argon coming out?

...so back to the Mantle

Hypothesis 1:

- We've met radioactivity inside the Earth before as an energy source, giving out heat.
- But what elements are involved in radioactive decay in rocks of mantle and crust?
- Most common radioactive isotope is potassium-40 $^{40}\text{K} \rightarrow ^{40}\text{Ar} + e^+$ ½-life ~1 billion years
- Argon is therefore still being produced in the rocks, and eventually escapes in volcanic gases

Hypothesis 2:

- Recent research has shown that argon and krypton are quite soluble in molten perovskite (MgSiO₃) which is the main component of the Earth's mantle, but xenon is not.
- In the Earth's early formation, xenon escaped from the molten proto-Earth, but argon was retained
- Argon may therefore still be coming out of its perovskite trap in the mantle, and eventually escaping in volcanic gases

What a story! Research will go on... and on....

