Geologic Evolution of Earth's Atmosphere

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

https://www.videoblocks.com/video/earth-sunset-spacewalk-view-from-space-station-r7dydlcsgjd23vml0

Lecture 1

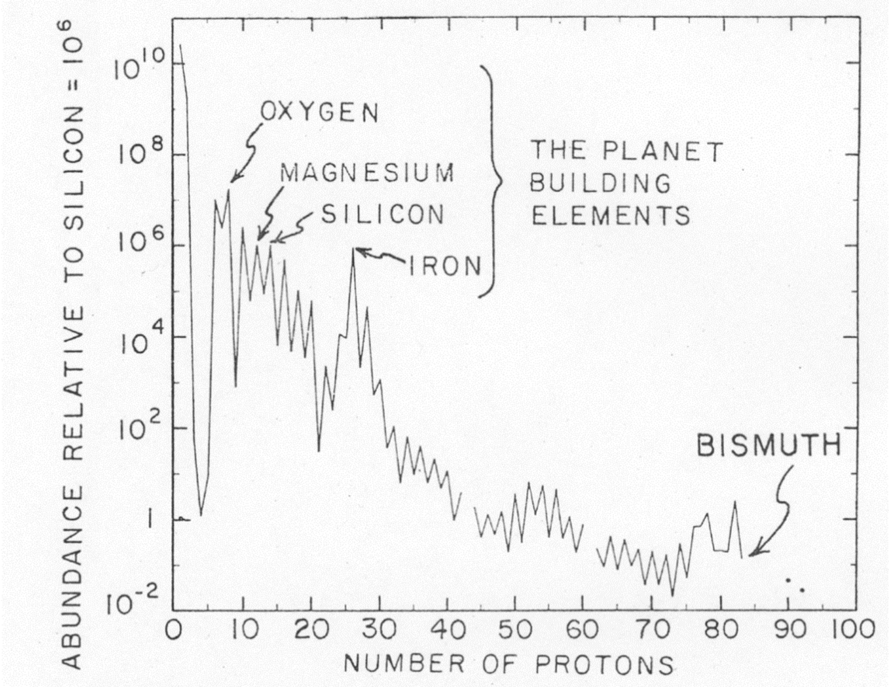
27 January 2022

Geological Evolution of Earth's Atmosphere:
"In the Beginning"

- **Assemblage of 92 natural elements**

- **Elemental composition of Earth basically unchanged over 4.5 Gyr**
  - Gravitational escape restricted to a few gases (H, He)
  - Extra-terrestrial inputs (comets, meteorites) relatively unimportant

- **Biogeochemical cycling of elements between reservoirs of Earth "system" determines atmospheric composition**

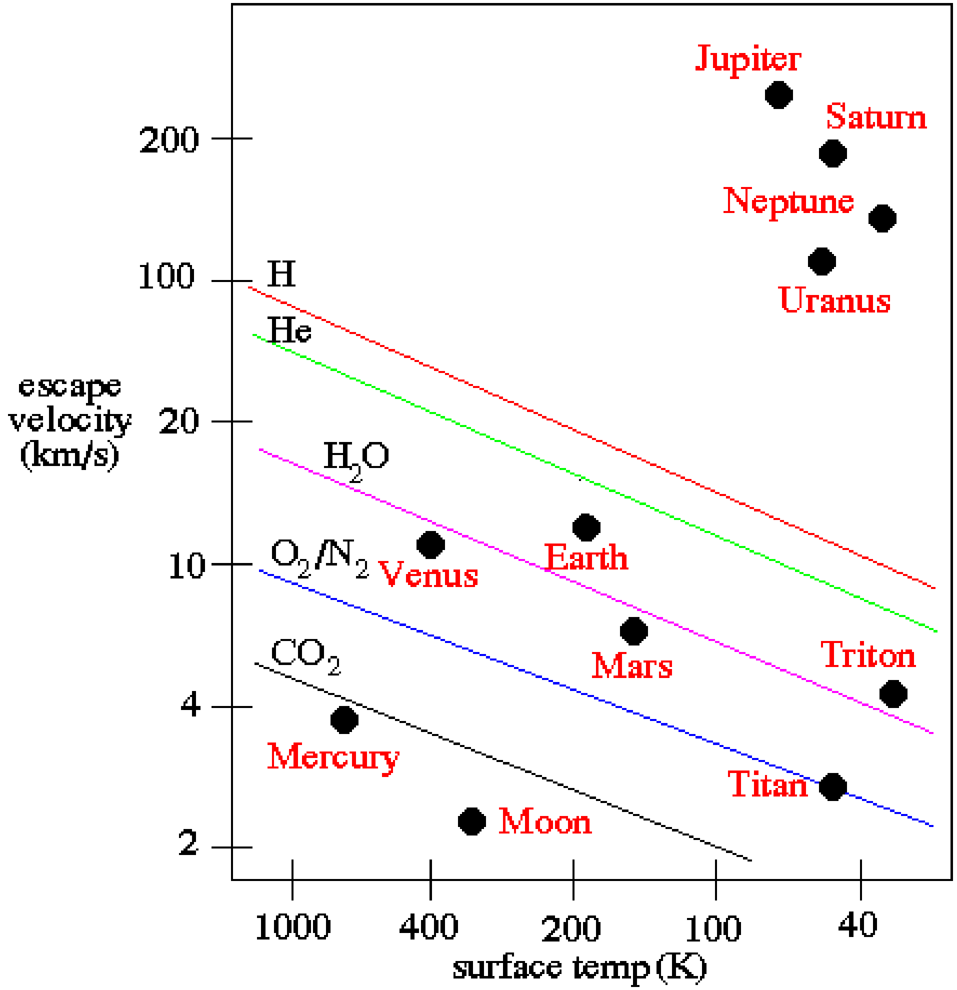


From "How to Build a Habitable Planet"
By W.S. Broecker, ELDIGIO Press, pg 57

Geological Evolution of Earth’s Atmosphere: *Earth, Mars, and Venus*

	Earth	Venus	Mars
Radius (km)	6400	6100	3400
Mass (10^{24} kg)	6.0	4.9	0.6
Albedo	0.3	0.8	0.22
Distance from Sun (A.U.)	1	0.72	1.52
Surface Pressure (atm)	1	91	0.007
Surface Temperature (K)	~15 °C	~ 460 °C	–140 °C to 20 °C
N_2 (mol/mol)	0.78	3.4×10^{-2}	2.7×10^{-2}
O_2 (mol/mol)	0.21	6.9×10^{-5}	1.3×10^{-3}
CO_2 (mol/mol)	3.7×10^{-4}	0.96	0.95
H_2O (mol/mol)	1×10^{-2}	3×10^{-3}	3×10^{-4}
SO_2 (mol/mol)	1×10^{-9}	1.5×10^{-4}	Nil
Cloud Composition	H_2O	H_2SO_4	Mineral Dust

Geological Evolution of Earth's Atmosphere: *Earth, Mars, and Venus*



http://abyss.uoregon.edu/~js/ast121/lectures/lec14.html

Geological Evolution of Earth's Atmosphere:
Earth is of course the water planet
The source of Earth's water has been unclear

A new study finds that Earth's water may have come from materials that were present in the inner solar system at the time the planet formed – instead of far-reaching comets or asteroids delivering such water. The findings published 28 Aug 2020 in Science suggest that Earth may have always been wet.

"Our discovery shows that the Earth's building blocks might have significantly contributed to the Earth's water," said lead author Laurette Piani. "Hydrogen-bearing material was present in the inner solar system at the time of the rocky planet formation, even though the temperatures were too high for water to condense."

The findings from this study are surprising because the Earth's building blocks are often presumed to be dry. They come from inner zones of the solar system where temperatures would have been too high for water to condense and come together with other solids during planet formation.

Enstatite chondrites have similar oxygen, titanium and calcium isotopes as Earth, and this study showed that their hydrogen and nitrogen isotopes are similar to Earth's, too. In the study of extraterrestrial materials, the abundances of an element's isotopes are used as a distinctive signature to identify where that element originated.

Press release: https://source.wustl.edu/2020/08/meteorite-study-suggests-earth-may-have-always-been-wet
Paper: https://www.science.org/doi/10.1126/science.aba1948

Geological Evolution of Earth's Atmosphere: *Outgassing*

H_2

N_2

CO_2

H_2O

oceans form

CO_2 dissolves

Outgassing

Life forms

4.5 Gy before present

4 Gy

3.5 Gy

0.4 Gy

present

Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Reducing Environment

Decreasing oxidation number (reduction reactions)

←

-3	0	+1	+2	+3	+4	+5
NH_3 **Ammonia**	N_2	N_2O **Nitrous oxide**	NO **Nitric oxide**	HONO **Nitrous acid** NO_2^- **Nitrite**	NO_2 **Nitrogen dioxide**	HNO_3 **Nitric acid** NO_3^- **Nitrate**

→

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons:
added to an element (– oxidation state) or
removed from an element (+ oxidation state)

Oxidation state of a compound: $\sum = -2 \times$ # O atoms + 1 $\times$ # H atoms;
Oxidation of element = Electrical Charge – $\sum$

Note: there are some exceptions to this rule, such as oxygen in peroxides

Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Reducing Environment

Decreasing oxidation number (reduction reactions)

←

-4	0	+2	+4
CH_4 **Methane**	CH_2O **Formaldehyde**	CO **Carbon Monoxide**	CO_2 **Carbon dioxide**

→

Increasing oxidation number (oxidation reactions)

Oxidation state represents number of electrons:
added to an element (– oxidation state) or
removed from an element (+ oxidation state)

Oxidation state of a compound: $\sum = -2 \times \#\text{ O atoms} + 1 \times \#\text{ H atoms}$;
Oxidation of element = Electrical Charge $- \sum$

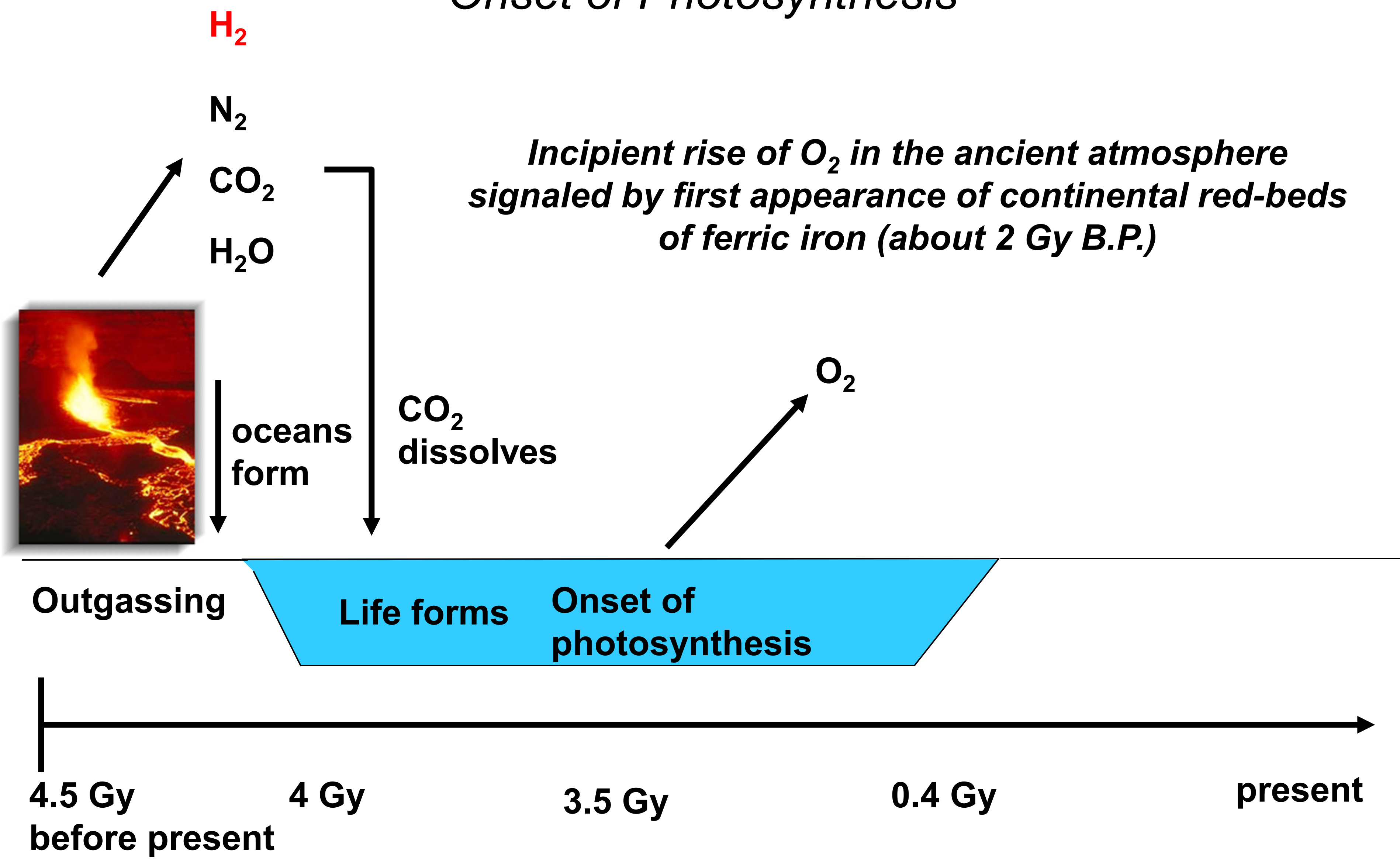
Note: there are some exceptions to this rule, such as oxygen in peroxides

Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Reducing Environment

How do we know early atmosphere was reducing ?

Why was a reducing environment important ?

Geological Evolution of Earth's Atmosphere:
Onset of Photosynthesis



Geological Evolution of Earth's Atmosphere: *Atmospheric O_2 on Geological Time Scales*

- **Rise of atmospheric O_2 linked to evolution of life:**

The rise of atmospheric O_2 that occurred ~2.4 billion years ago was the greatest *environmental* crisis the Earth has endured. [O_2] rose from one part in a million to one part in five: from 0.00001 to 21% ! Earth's original biosphere was like an alien planet. Photosynthetic bacteria, frantic for hydrogen, discovered water and its use led to the build up of atomic O, a toxic waste product.

Many kinds of microbes were wiped out. O and light together were lethal. The resulting O-rich environment tested the ingenuity of microbes, especially those non-mobile microorganisms unable to escape the newly abundant reactive atmospheric gas. The microbes that survived invented various intracellular mechanisms to protect themselves from and eventually exploit this most dangerous pollutant.

Lynn Margulis and Dorion Sagan, Microcosmos: Four Billion Years of Microbial Evolution, 1986

The rise of atmospheric oxygen led to something else critical to "life as we know it" − what did rising [O_2] lead to ?!?

Geological Evolution of Earth's Atmosphere: *Atmospheric O_2 on Geological Time Scales*

- **Rise of atmospheric O_2 linked to evolution of life:**

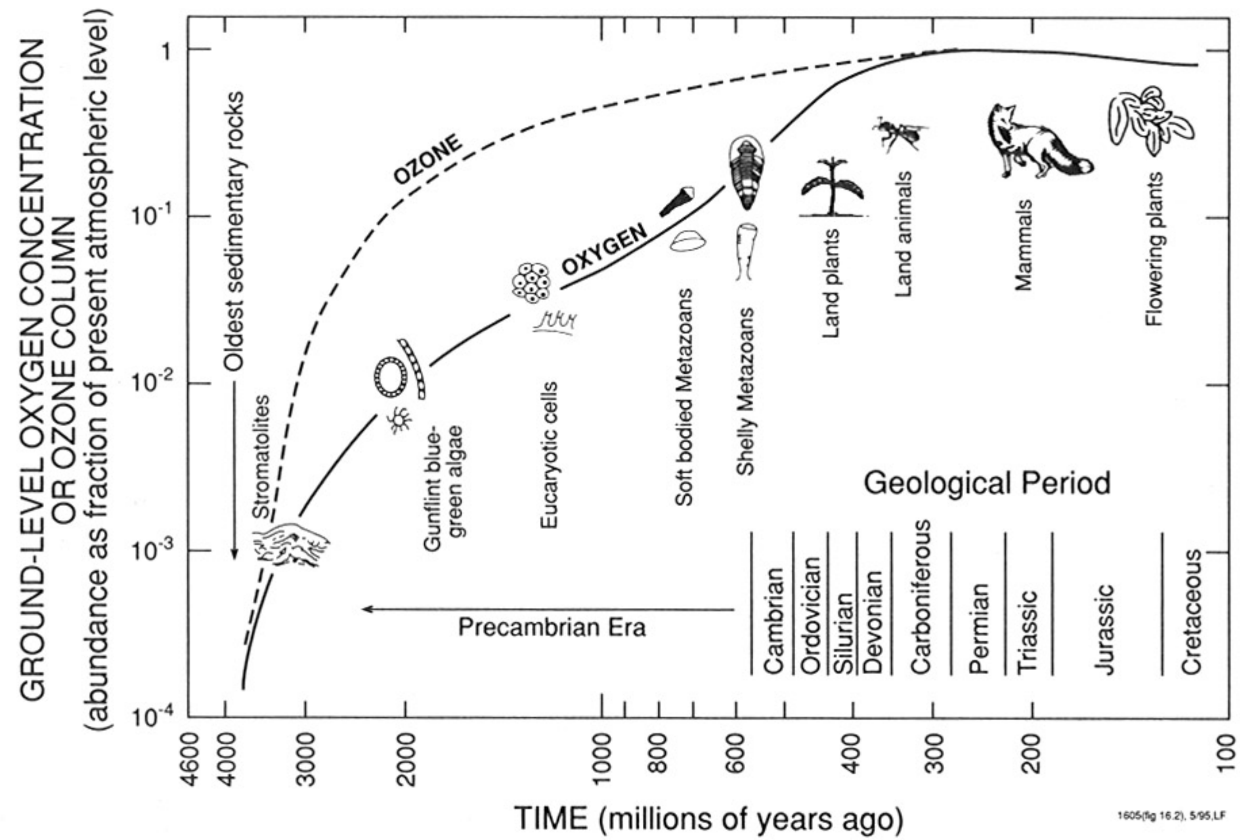


Figure 16.3. *Probable evolution of the oxygen and ozone abundance in the atmosphere (fraction of present levels) during the different geological periods of the Earth's history (Wayne, 1991; reprinted by permission of Oxford University Press).*

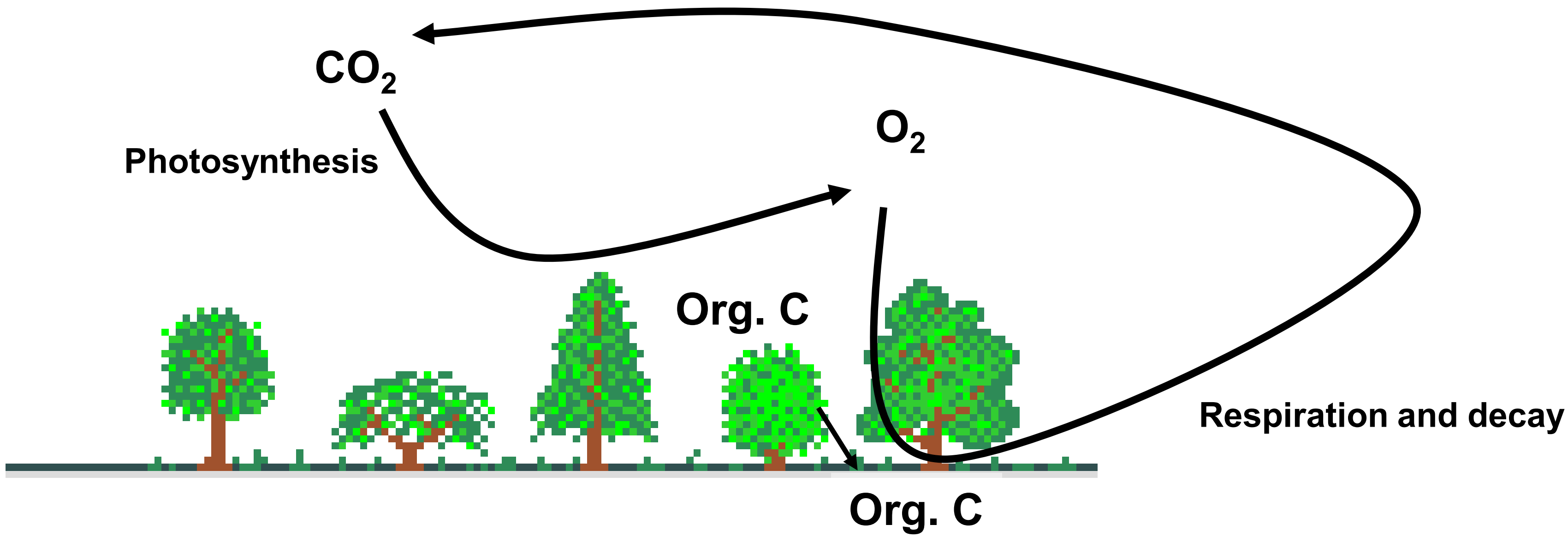
Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

- **Photosynthesis: Source of O_2**

$$6CO_2 + 6H_2O + \text{energy} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

- **Respiration and Decay: Sink of O_2**

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$

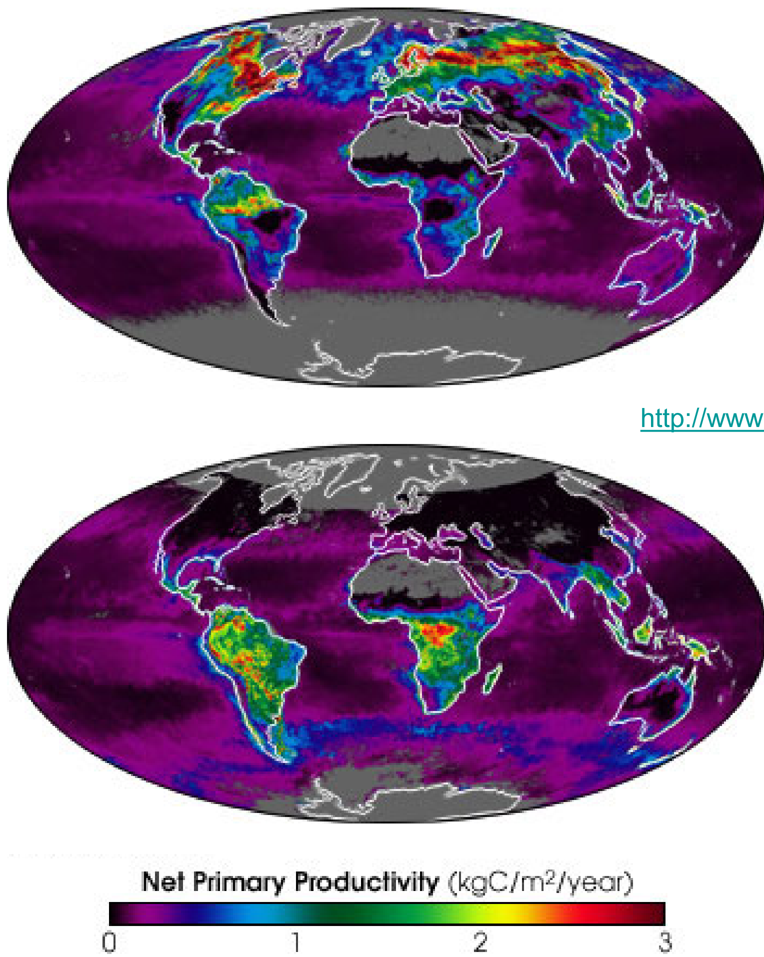


Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

- **Net primary productivity of organic matter:**
  $6\ CO_2 + 6\ H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\ O_2$ is ~ 57×10^{15} g C yr^{-1}

Imhoff *et al.*, *Nature*, 2004

http://www.globalcarbonproject.org/science/figures/FIGURE9.htm



Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

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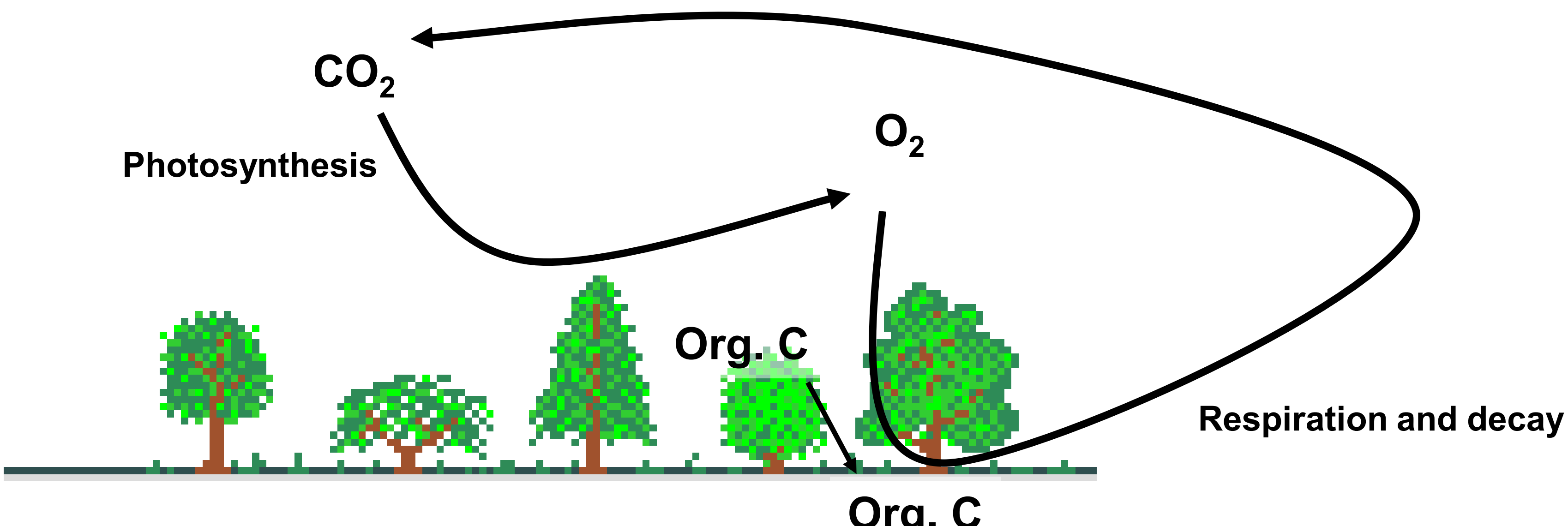
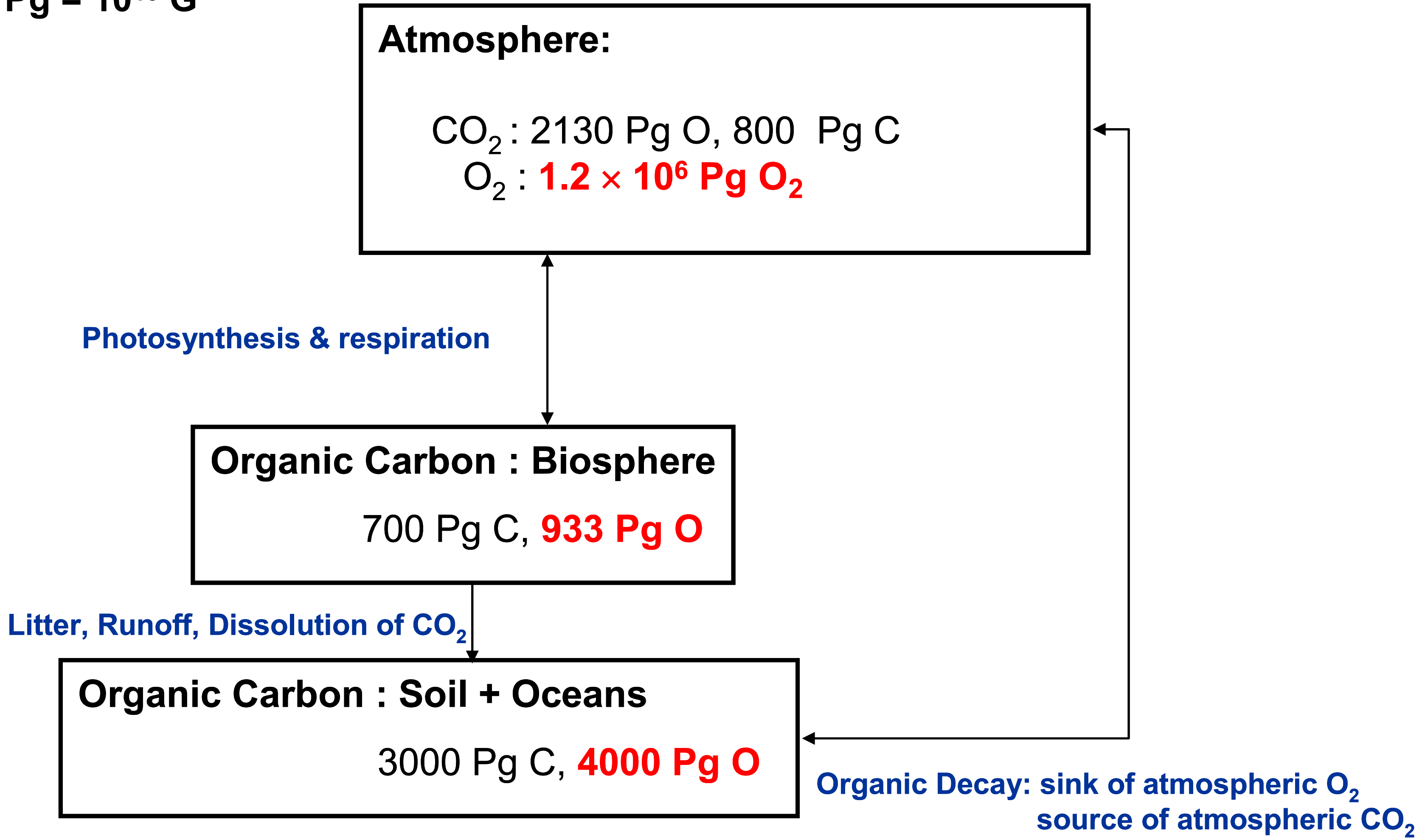
  $6\ CO_2 + 6\ H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\ O_2$ is ~ 57×10^{15} g C yr^{-1}
  Production of atmospheric O_2 is therefore ~152×10^{15} g O_2 yr^{-1} Flux
- **Mass O_2 in atmosphere = $0.21 \times (5.2 \times 10^{21}\ g) \times (32 / 28.8) \approx 1.2 \times 10^{21}$ g** Amount
- **Lifetime of atmospheric O_2 due to biology = Amount / Flux**



Geological Evolution of Earth's Atmosphere: *Oxygen and Carbon Reservoirs*

1 Pg = 10^{15} G



Atmospheric O_2 reservoir much larger than O_2 content of biosphere, soils, and ocean; therefore, some *other process* must control atmospheric O_2

Geological Evolution of Earth's Atmosphere:
Oxygen Reservoirs & Pathways

1 Pg = 10^{15} G

Atmosphere:

O_2 : 1.2×10^6 Pg O_2

Burial of organic matter is source of atmospheric O_2:

$6CO_2 + 6\,H_2O$ + Energy $\rightarrow$

$C_6H_{12}O_6$ (buried) + $6O_2$ (atmosphere)

O_2 Lifetime $\approx$ 4 million years

Sediments: Buried Organic Carbon

O_2 : ~32×10^6 Pg O

Weathering of mantle is sink of atmospheric O_2:

For example:

$FeS_2 + 7/2\,O_2 + H_2O \rightarrow Fe^{3+} + 2\,SO_4^{2-} + 2\,H^+$.

Crust and Mantle: Oxides of Fe, Si, S, Mg, etc:

FeO, Fe_2O_3, $FeSiO_3$, SiO_4, MgO, etc

This is where the bulk of the oxygen resides!

Geological Evolution of Earth's Atmosphere: *Atmospheric O_2 on Geological Time Scales*

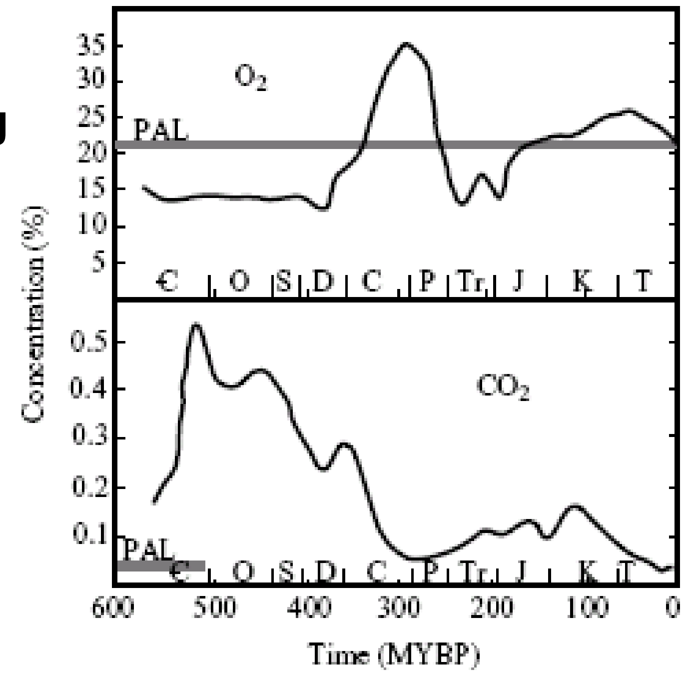
- **Rise of atmospheric O_2 linked to evolution of life:**
  - **400 My B.P. O_2 high enough to form an ozone layer**
  - **400 to 300 My B.P.: first air breathing lung fish & primitive amphibians**

- **On geological timescales, level of O_2 represents balance between burial of organic C & weathering of sedimentary material:**

  (see Chapter 12, "Evolution of the Atmosphere" in *Chemistry of the Natural Atmosphere* by P. Warneck (2nd ed) for an excellent discussion)

- **Present atmosphere is oxidizing:**

  $CH_4 \Rightarrow CO_2$ with time scale of ~9 years



From R. Dudley, Atmospheric O_2, Giant Paleozoic Insects, and the Evolution of Aerial Locomotor Performance, *J. Exper. Biol.,* 201, 1043, 1998.

Geological Evolution of Earth's Atmosphere:
Atmospheric CO_2 on Geological Time Scales

~500 to 300 My B.P.

- **Development of vascular land plants**
- **Plants became bigger and bigger and less reliant on water**
- **Once buried, lignin in woody material resists decay**
- **Burial rate of terrestrial plant matter increases dramatically:**
  (evidence : $\delta^{13}C$ analysis)
- **Past burial rate of vascular plant material may have been much higher than present, due to the lack (way back when) of abundant bacteria, fungi, and small soil animals that now recycle plant matter**

Non-vascular: Bryophytes

Vascular: Pteridophytes

Geological Evolution of Earth's Atmosphere: *Atmospheric CO_2 on Geological Time Scales*

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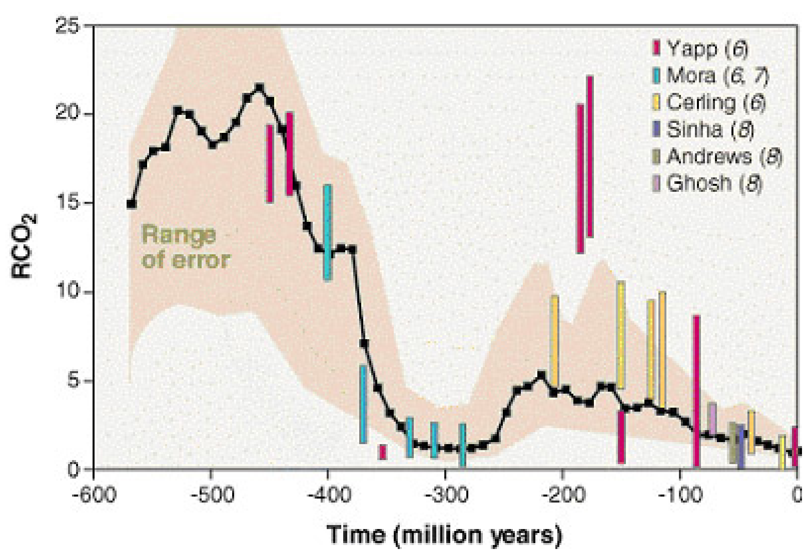


From R. Berner, *Science,* 276, 544, 1997.

Geological Evolution of Earth's Atmosphere: *Precursors of Modern Day World*

N_2

CO_2

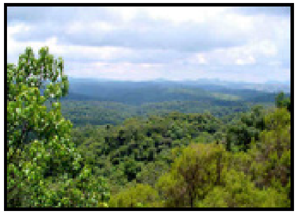
H_2O

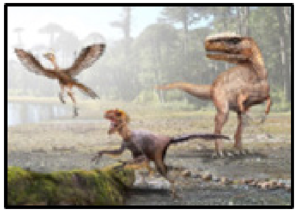
oceans form

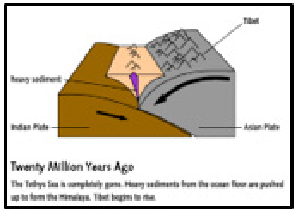
CO_2 dissolves

O_2

O_2 reaches current levels;
tree life flourishes;
animal life invades continents;
dinosaurs roam the Earth;
rise of Himalayas







Outgassing

Life forms

Onset of photosynthesis

4.5 Gy before present — **4 Gy** — **3.5 Gy** — **0.4 Gy** — **present**

Geological Evolution of Earth's Atmosphere: CO_2 and Temperature

What message were we trying to convey?

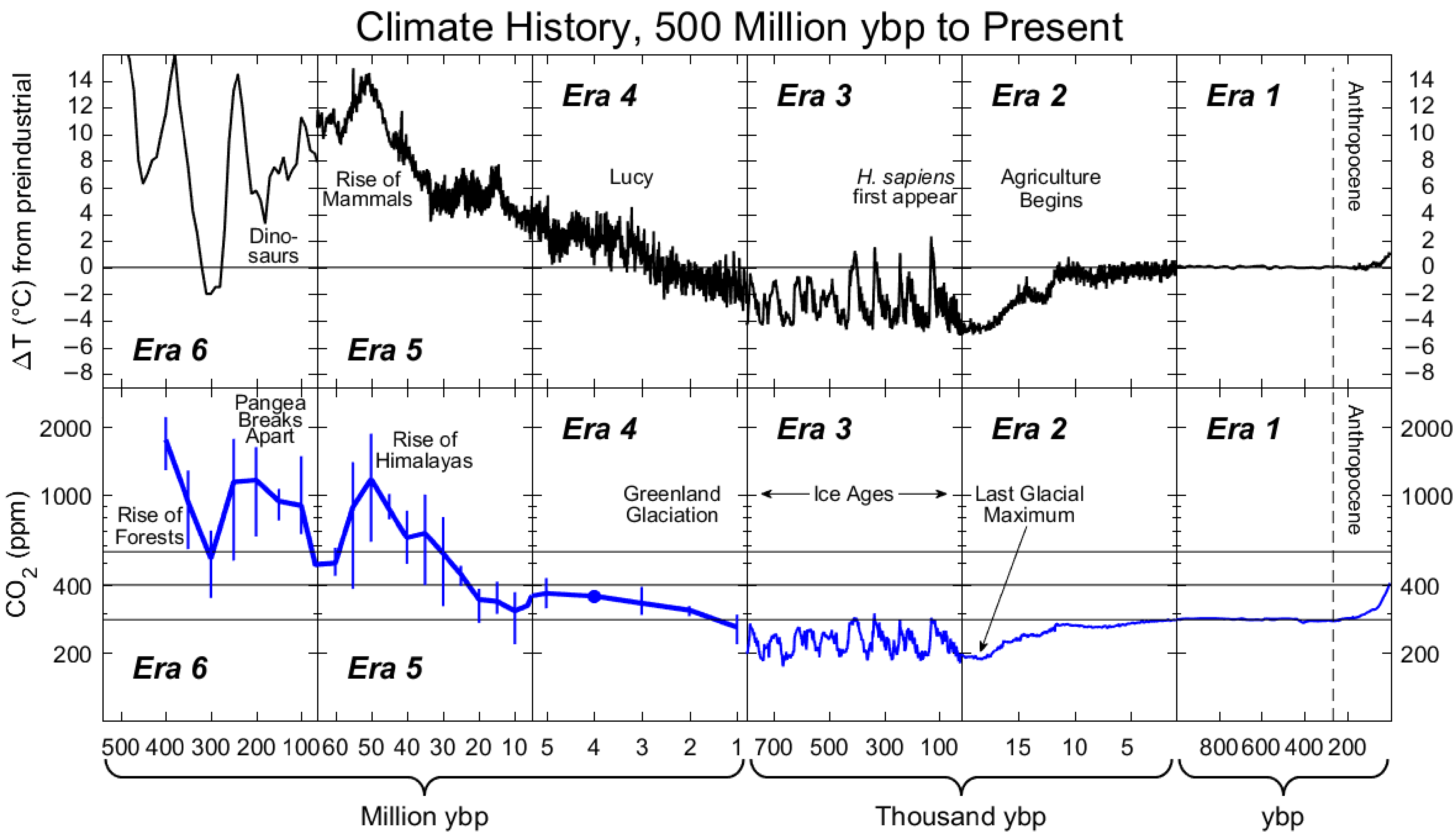
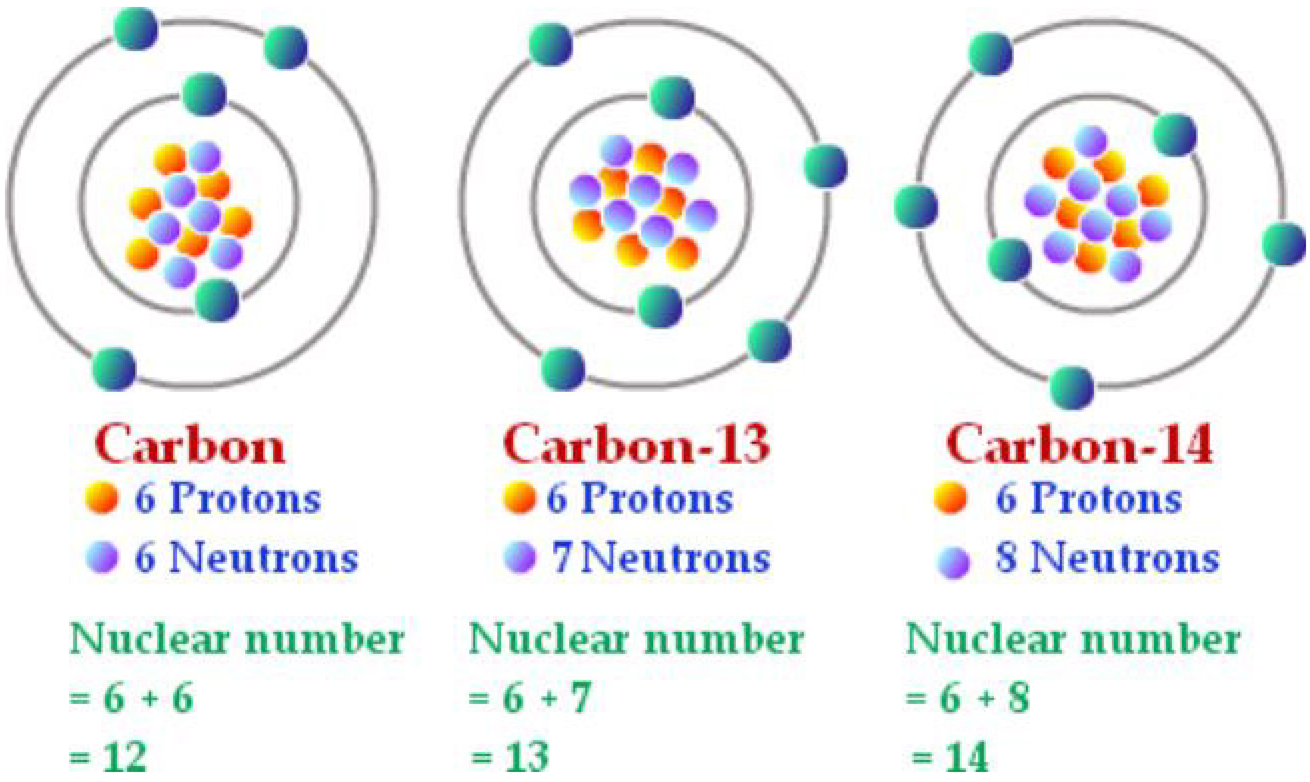


Fig 1.1, *Paris Beacon of Hope*

Geological Evolution of Earth's Atmosphere: One Day, ***Everything Changed***

Biology prefers light forms of carbon:



https://experiment.com/u/iA41fA

Geological Evolution of Earth's Atmosphere: One Day, ***Everything Changed***

By understanding how the carbon isotopic ratio of the world's surface waters changed at the K-T boundary, as recorded by the shells of preserved oceanic organisms, we could compute the fraction of the world's biosphere that must have burned on this really bad day (or soon thereafter):

Carbon isotopic evidence for biomass burning at the K-T boundary

A new interpretation of existing carbon isotopic data combined with results from a biogeochemical model suggests that burning of terrestrial biomass occurred on a global scale at the Cretaceous-Tertiary (K-T) boundary. Carbon isotopic ratios from planktonic and benthic microfossils across the K-T boundary reveal not only a breakdown in the normal surface-water to deep-water gradient of $^{13}C/^{12}C$, but also a reversal at the boundary. This reversal cannot be explained by the cessation of primary production alone. We propose that combustion of terrestrial biomass with subsequent transfer of isotopically light carbon to surface waters is the most likely cause of this anomaly. A biogeochemical model is used to quantify the extent of burning at the boundary: combustion of roughly 25% of the above-ground biomass at the end of the Cretaceous is necessary to account for the observed isotopic signal.

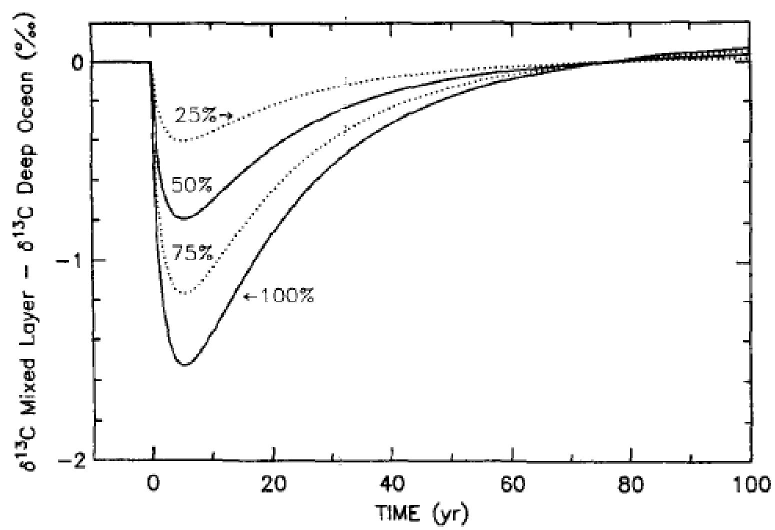
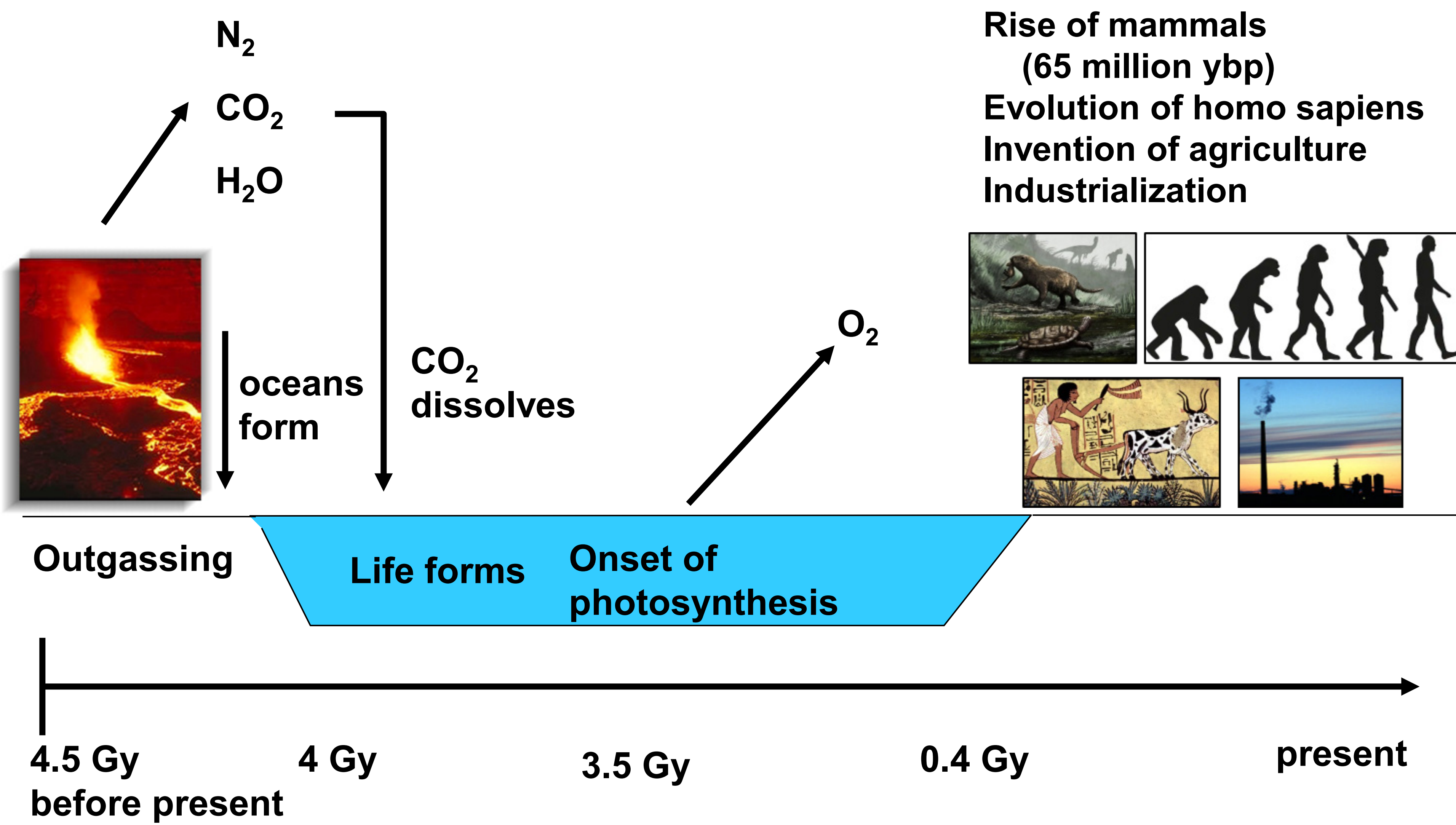


Figure 2. Variation of surface-water to deep-water gradient of $\delta^{13}C$ vs. time for simulations of biomass combustion, assumed to occur instantaneously at time zero. Results are shown for burning 25%, 50%, 75%, and 100% of above-ground biomass (10^{18} g C; $\delta^{13}C = -25.7‰$) at end of Cretaceous assuming combustion efficiency of 50% (i.e., model result for 100% combustion corresponds to injection of half of above-ground biomass carbon into atmosphere as CO_2 at time zero).

Ivany and Salawitch, *Geology*, 1993
Link to this paper appears in auxiliary reading for today's class

Geological Evolution of Earth’s Atmosphere: *Human Influence*



Geological Evolution of Earth's Atmosphere: *Human Influence*

What message were we trying to convey?

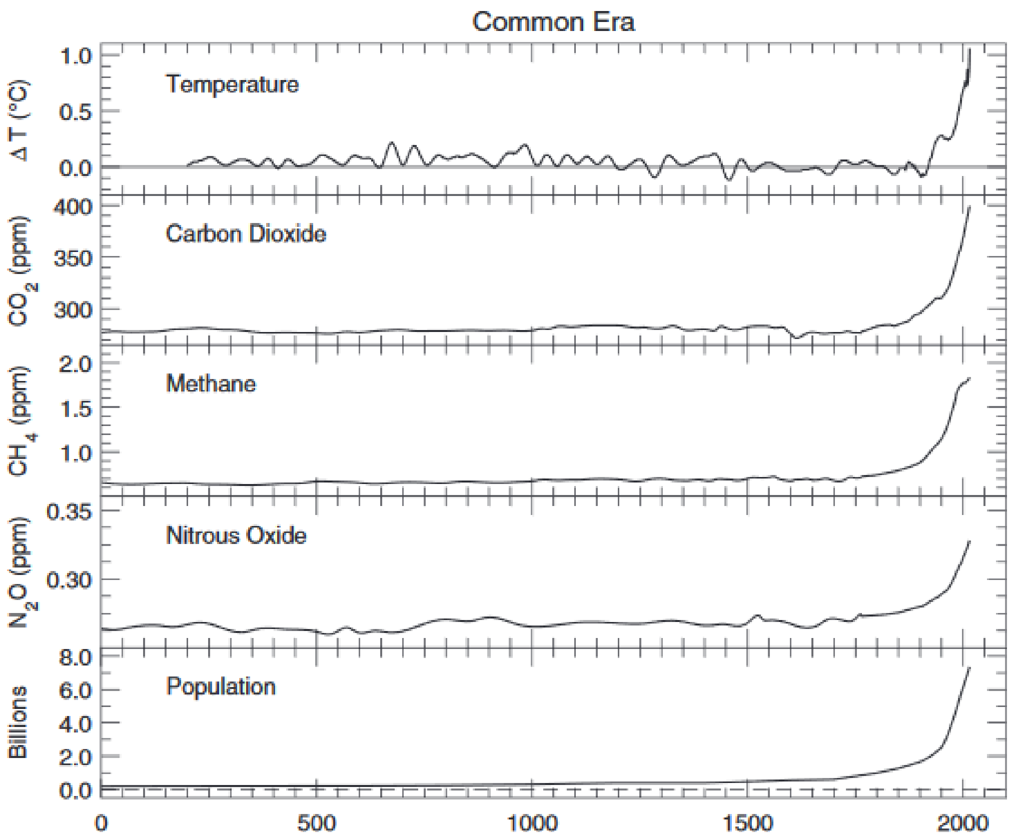
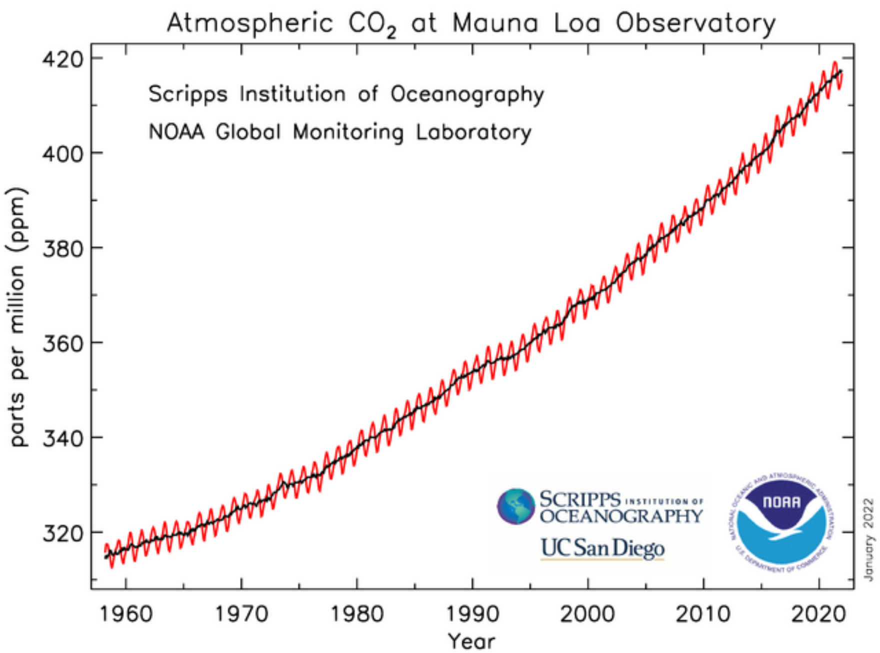


Fig. 1.2 Temperature, GHGs, and population, Common Era. Time series of Earth's global mean surface temperature anomaly (ΔT) relative to pre-industrial baseline (1850–1900 mean) (Jones and Mann 2004; Jones et al. 2012), the atmospheric mixing ratio of CO_2, CH_4, and N_2O (MacFarling Meure et al. 2006; Ballantyne et al. 2012; Dlugokencky et al. 2009; Montzka et al. 2011) and global population (Klein Goldewijk et al. 2010; United Nations 2015) over the Common Era. See Methods for further information

Earth's Atmosphere – Effect of Humans

CO_2: ~415 parts per million (ppm) and rising !



Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
https://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png

Human drivers of global warming over the last millennium

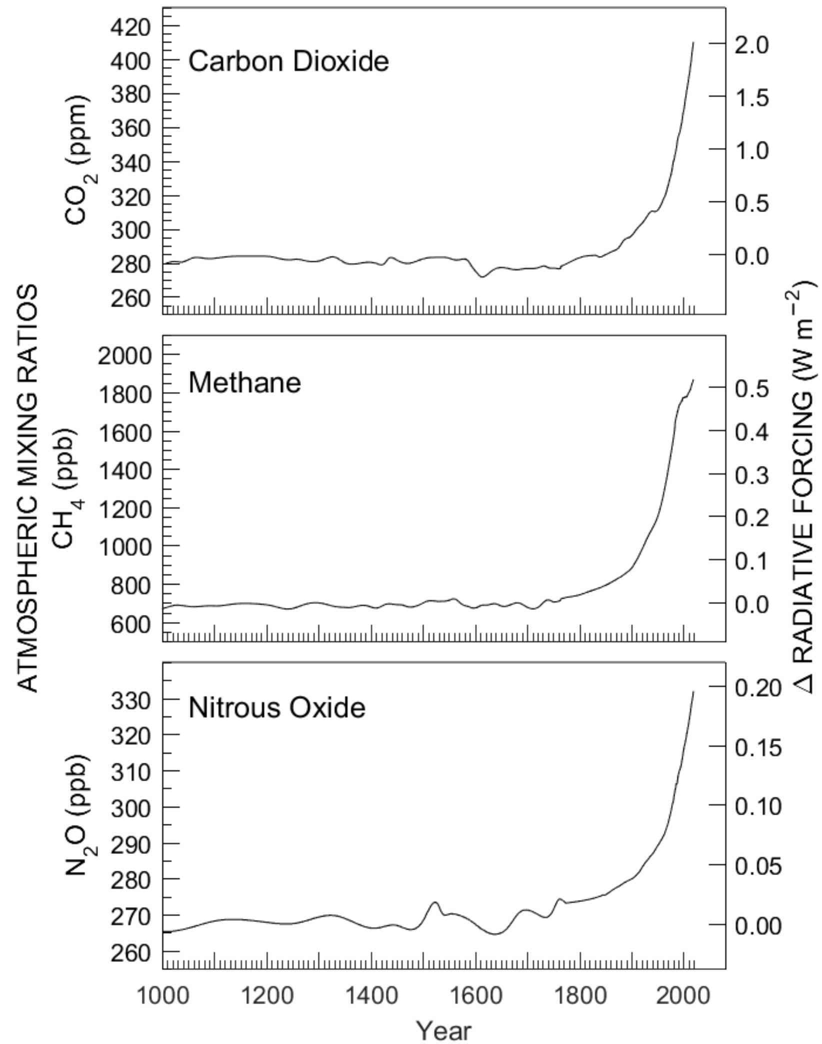
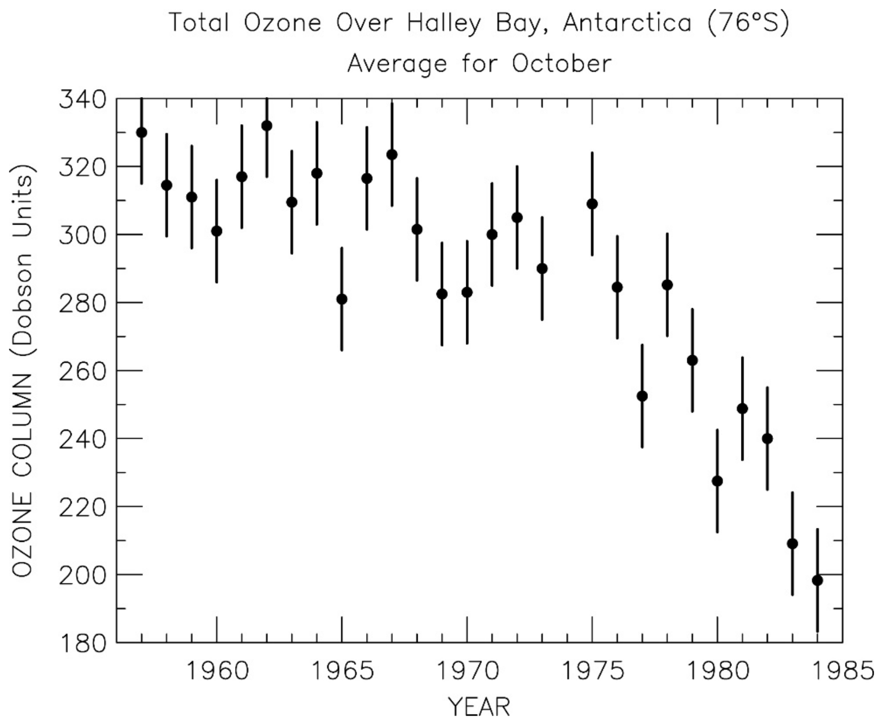


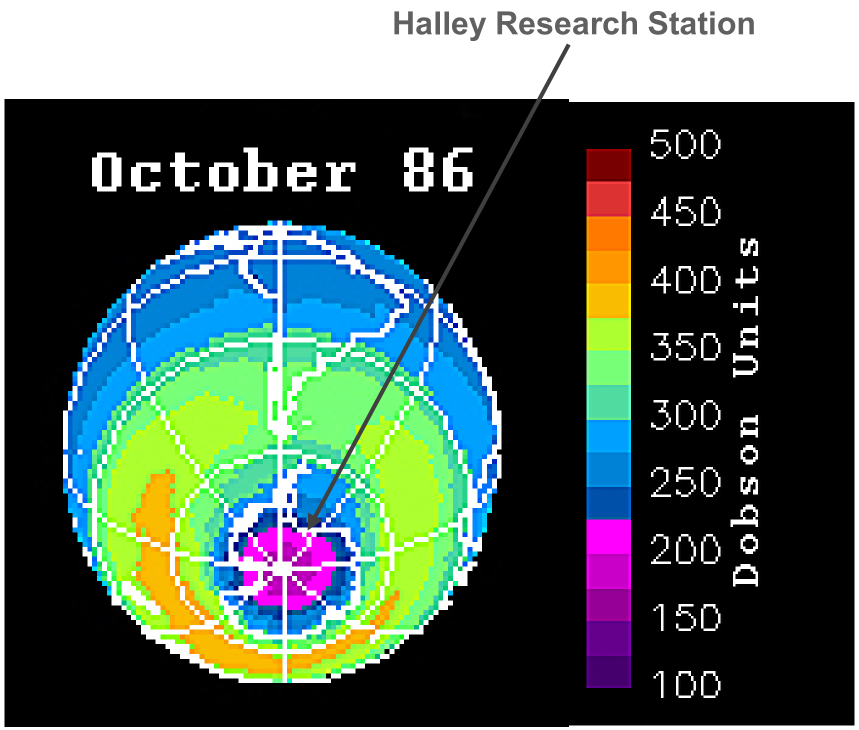
Figure courtesy Brian Bennett, Univ of Md

Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation



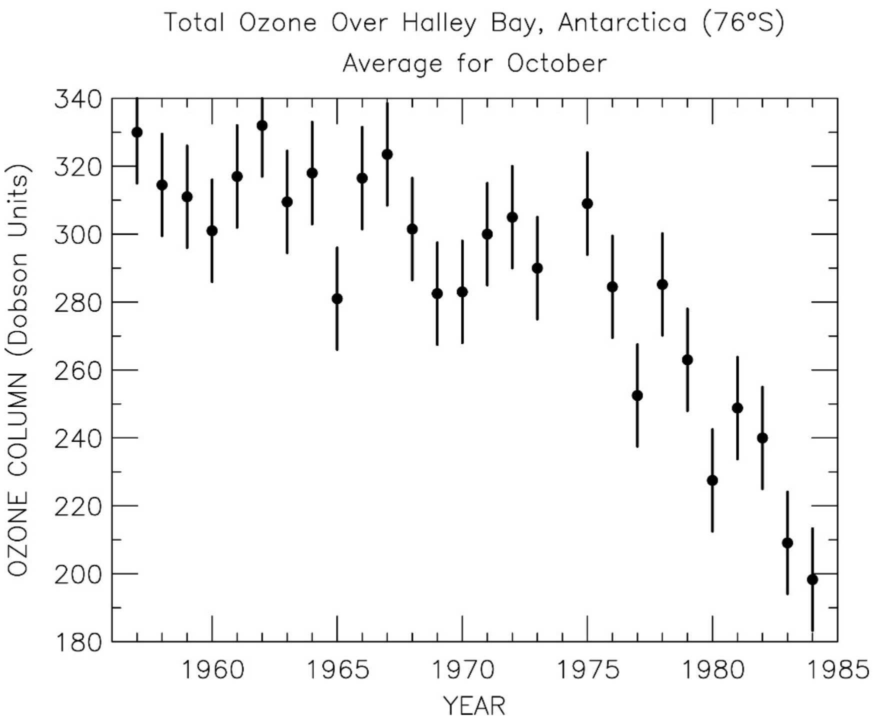
After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.



Stolarski *et al*., Nature, 1986.

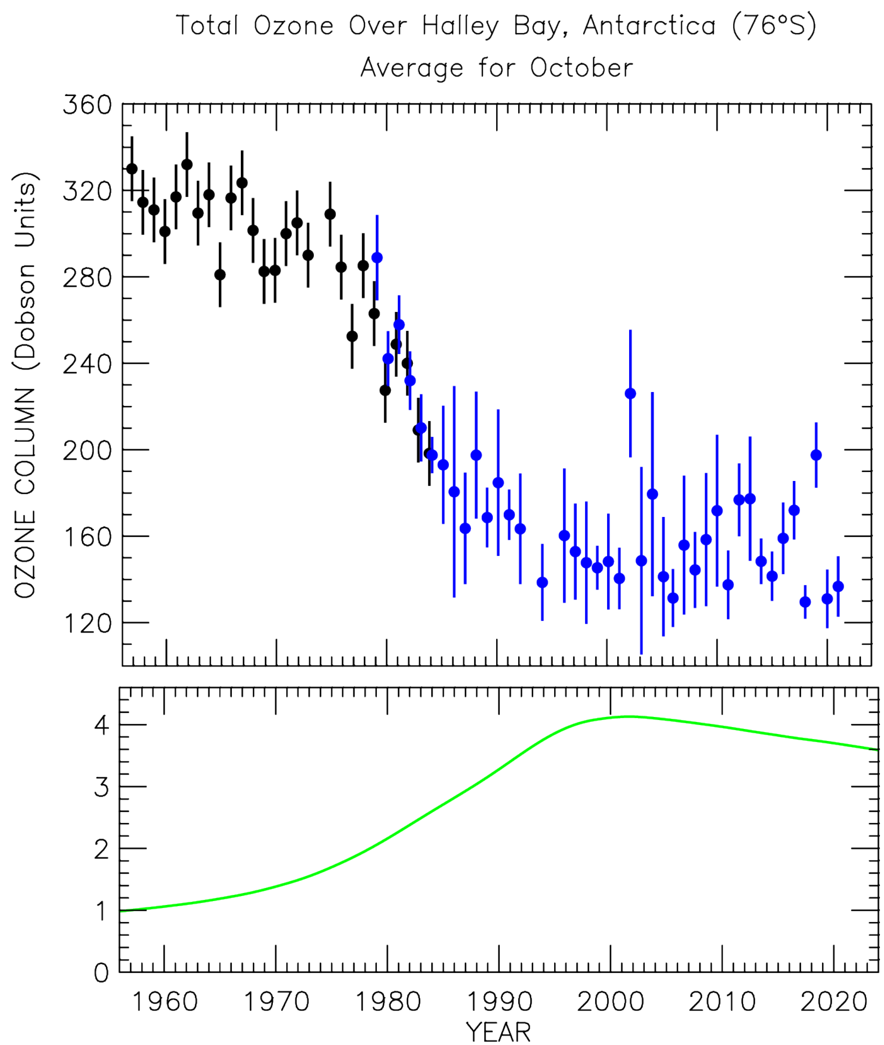
Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation



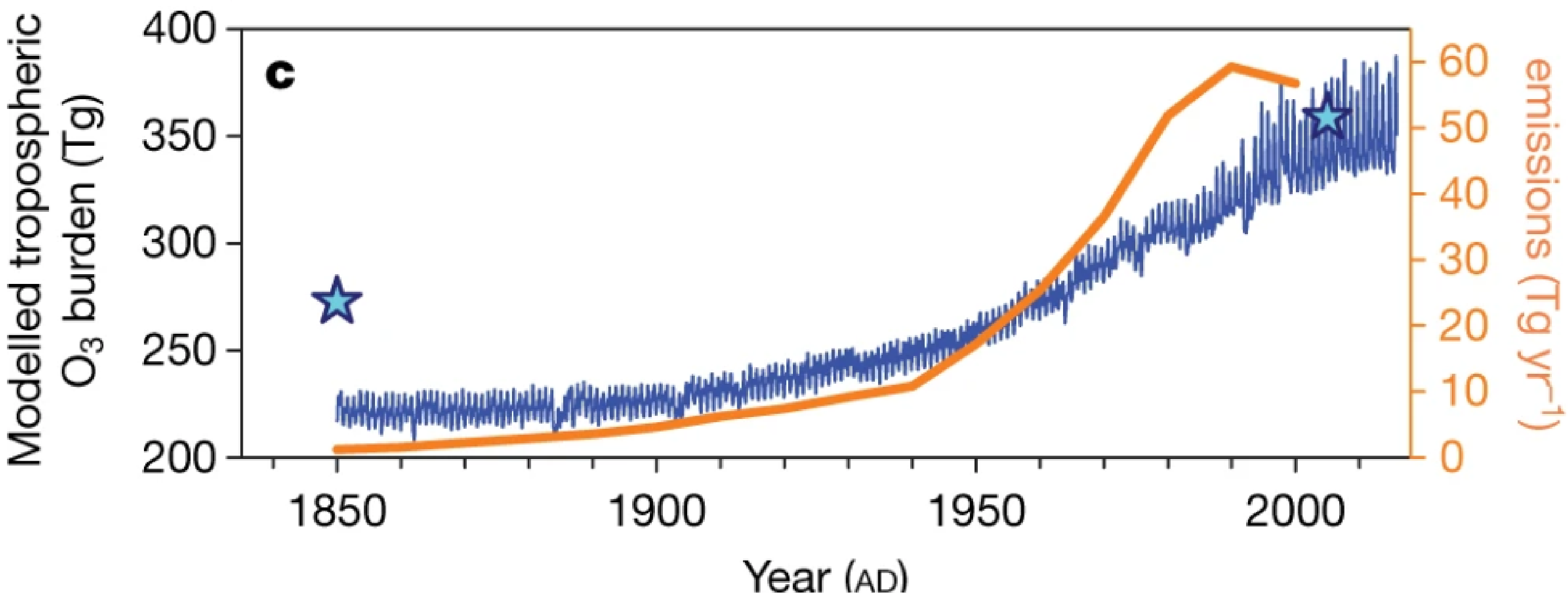
After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.

Update



Earth's Atmosphere – Effect of Humans

Tropospheric Ozone – oxidant, lung irritant, harmful to crops



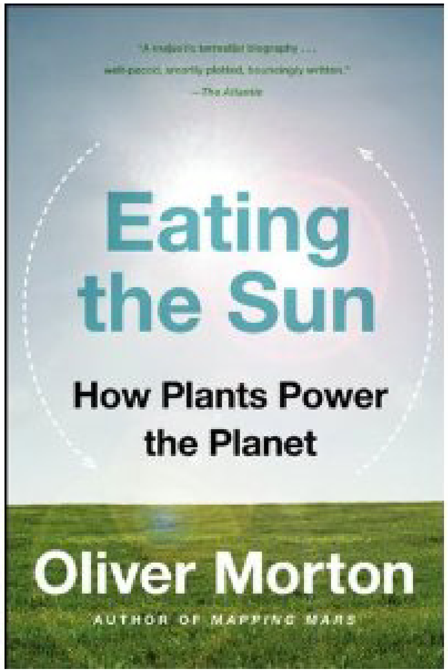
Modelled increase in tropospheric O_3 burden from the GEOS-Chem/MERRA2 model (cyan stars) and GISS-E2.1 model (blue line), as well as estimates of historical emissions of NO_x (orange line).

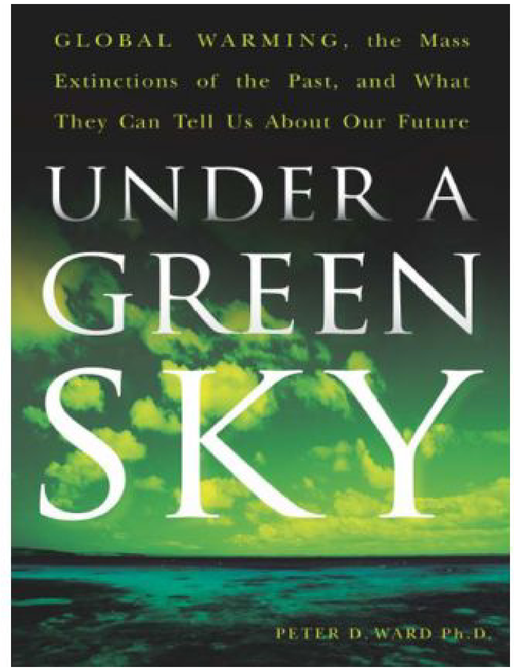
Yueng *et al.*, *Nature*, 2019

https://www.nature.com/articles/s41586-019-1277-1

Source Material

These books are a great resource for how photosynthesis works as well as the history of atmospheric composition





http://www.amazon.com/Eating-Sun-Plants-Power-Planet/dp/0007163657/ref=sr_1_1?s=books&ie=UTF8&qid=1359325940&sr=1-1&keywords=eating+the+sun

http://www.amazon.com/Under-Green-Sky-Warming-Extinctions/dp/0061137928/ref=sr_1_1?s=books&ie=UTF8&qid=1359326345&sr=1-1&keywords=under+a+green+sky

and provided some of the source material for much of this lecture

Next Lecture: Course Overview

https://www2.atmos.umd.edu/~rjs/class/spr2022/

Most Visited Getting Started Most Visited Getting Started Business Roundtable Server Not Found

2. Schedule

Date	Lecture Topic	Required Reading	Admis. Tickets	Lecture Notes	Problem Sets*	Additional Readings	Learning Outcome
01/25	Class Overview	No reading for first meeting	No AT	Lecture 0 Video			No Quiz
01/27	Geological Evolution of Earth's Atmosphere	Paris Beacon of Hope Sec 1.1, 1.2 (intro), and 1.2.1 (11.5 pages)	AT 1	Lecture 1 Video		Ivany and Salawitch, *Geology*, 1993 NOVA: The Day The Dinosaurs Died	Quiz 1
02/01	Overview of Global Warming, Air Quality, & Ozone Depletion	IPCC 2007 FAQ (1.1, 1.2, 1.3, 2.1, & 3.1) (11 pages) EPA AQI Brochure (11 pages) 20 QAs Ozone (Q1, 2, 7, & 14) (11 pages) Paris Beacon of Hope Sec 1.2.2 (3 pages)	AT 2	Lecture 2 Video		Kerr, *Science*, 2007 * Bell *et al.*, *EHP*, 2006 * Montzka *et al.*, *Nature*, 2018 Naming Convention for CFCs & Halons Entire IPCC 2007 FAQ Entire 20 QAs Ozone Movie Clip	Quiz 2

Readings: IPCC 2007 FAQ 1.1, 1.2, 1.3, 2.1, & 3.1 (11 pages)
EPA Air Quality Guide (11 pages)
20 QAs Ozone Layer Q1, 2, 7, and 14 (11 pages)
Paris Beacon of Hope, Sect 1.2.2 (3 pages)

Note: 36 pages, about our norm

Admission Ticket for Lecture 2 is posted on ELMS