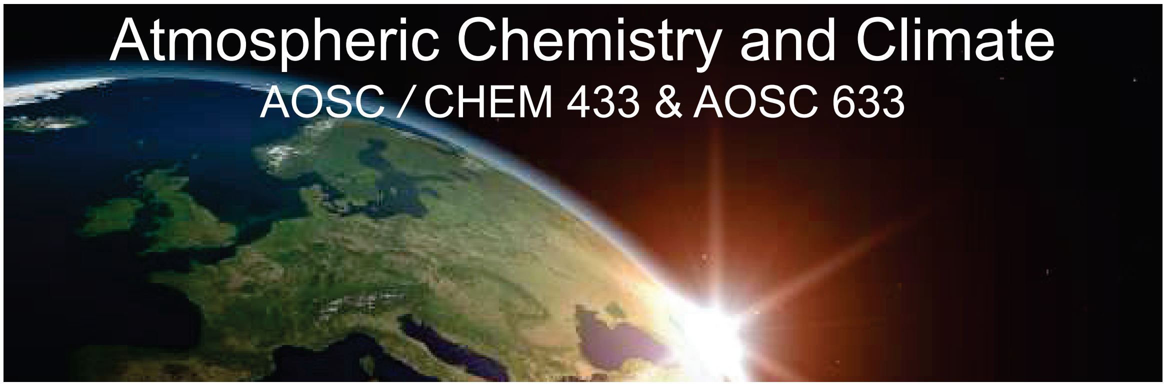


Atmospheric Chemistry and Climate

AOSC / CHEM 433 & AOSC 633

Ross Salawitch (rjs@atmos.umd.edu): Professor
Walt Tribett (wtribett@umd.edu): Teaching Assistant

Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

Required Textbook: *Chemistry in Context: Applying Chemistry to Society*,
American Chemical Society ⇒ **7th Edition !**

Supplemental Texts:

Global Warming: The Complete Briefing 5th Edition by John Houghton

Paris Climate Agreement: Beacon of Hope by Ross Salawitch, Tim Canty, Austin Hope, Walt Tribett, and Brian Bennett

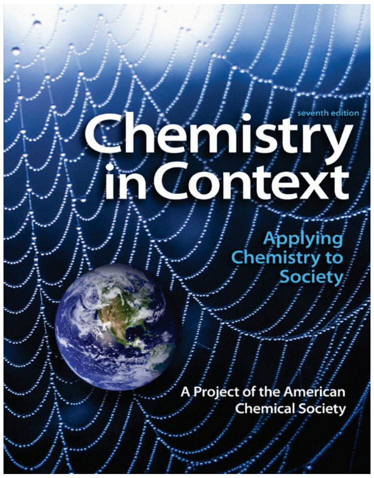
Beyond Oil and Gas: The Methanol Economy by George A. Olah, Alain Goeppert, and G. K. Surya Prakash

Green Chemistry: An Inclusive Approach, edited by Béla Török and Timothy Dransfield
(graduate students will be assigned two chapters)

Lecture 1

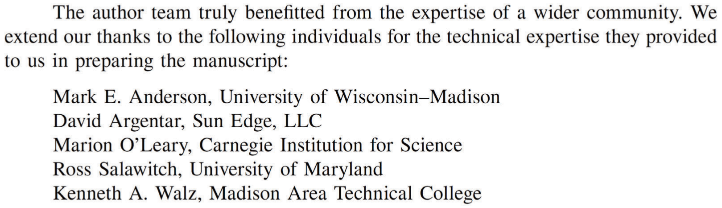
31 January 2019

Required Textbook: *Chemistry in Context: Applying Chemistry to Society*,
American Chemical Society ⇒ **7th edition !**



Chemistry in Context : Applying Chemistry to Society, 7/e

American Chemical Society (ACS)
Catherine H. Middlecamp, University of Wisconsin--Madison
Steven W. Keller, University of Missouri--Columbia
Karen L. Anderson, Madison Area Technical College
Anne K. Bentley, Lewis & Clark College
Michael C. Cann, University of Scranton
Jamie P. Ellis, The Scripps Research Institute

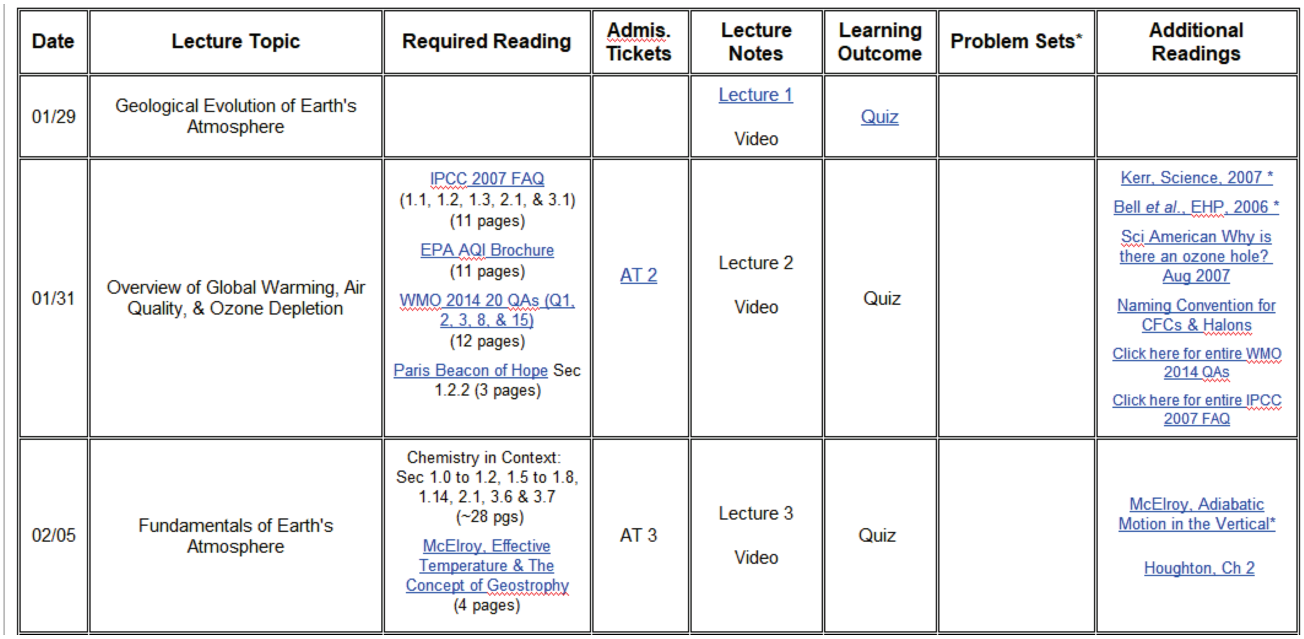


The author team truly benefitted from the expertise of a wider community. We extend our thanks to the following individuals for the technical expertise they provided to us in preparing the manuscript:

Mark E. Anderson, University of Wisconsin–Madison
David Argentar, Sun Edge, LLC
Marion O'Leary, Carnegie Institution for Science
Ross Salawitch, University of Maryland
Kenneth A. Walz, Madison Area Technical College

- Active used book market for 7th edition, since release of 8th edition
- Changes from edition to edition are minor: we will use 7th edition to save you $$$
- Can rent for $20, refundable at end of semester *upon return of book*
- If you collect text books for future reference, can find many used copies of the 7th edition for on-line purchase at a reasonable price. Please note this book is more of a "tutorial" than an indispensable reference book for your personal library, so probably best to first rent, see if the book is worth buying, and if you choose to buy you are welcome to return the rental early

Class Website



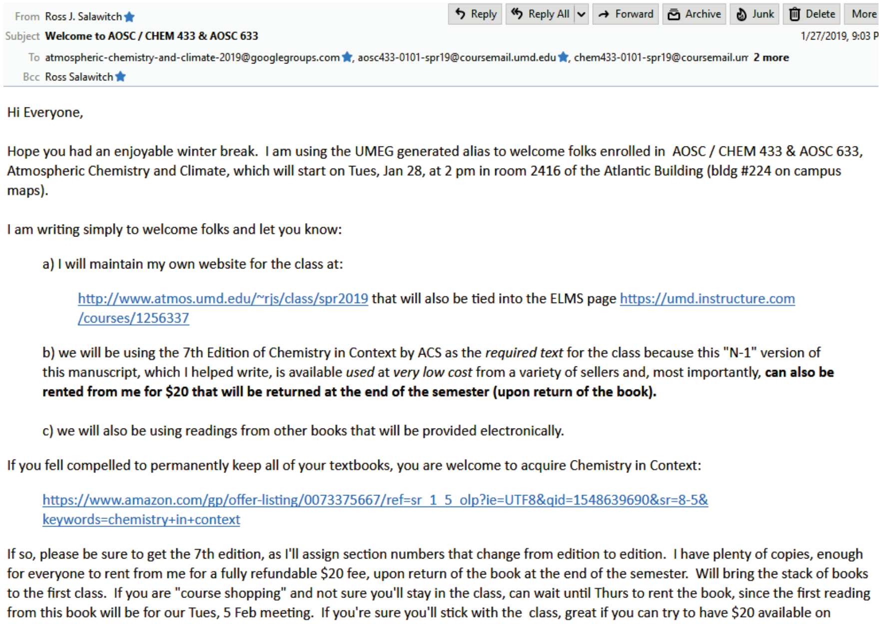
Date	Lecture Topic	Required Reading	Admis. Tickets	Lecture Notes	Learning Outcome	Problem Sets*	Additional Readings
01/29	Geological Evolution of Earth's Atmosphere			Lecture 1 Video	Quiz		
01/31	Overview of Global Warming, Air Quality, & Ozone Depletion	IPCC 2007 FAQ (1.1, 1.2, 1.3, 2.1, & 3.1) (11 pages) EPA AQI Brochure (11 pages) WMO 2014 20 QAs (Q1, 2, 3, 8, & 15) (12 pages) Paris Beacon of Hope Sec 1.2.2 (3 pages)	AT 2	Lecture 2 Video	Quiz		Kerr, Science, 2007 * Bell *et al.*, EHP, 2006 * Sci American Why is there an ozone hole? Aug 2007 Naming Convention for CFCs & Halons Click here for entire WMO 2014 QAs Click here for entire IPCC 2007 FAQ
02/05	Fundamentals of Earth's Atmosphere	Chemistry in Context: Sec 1.0 to 1.2, 1.5 to 1.8, 1.14, 2.1, 3.6 & 3.7 (~28 pgs) McElroy, Effective Temperature & The Concept of Geostrophy (4 pages)	AT 3	Lecture 3 Video	Quiz		McElroy, Adiabatic Motion in the Vertical* Houghton, Ch 2

http://www.atmos.umd.edu/~rjs/class/spr2019

Class file is psswrd protected using ATL2416

Class Organization

How many students got this email?



From Ross J. Salawitch
Subject **Welcome to AOSC / CHEM 433 & AOSC 633**
1/27/2019, 9:03 P
To atmospheric-chemistry-and-climate-2019@googlegroups.com, aosc433-0101-spr19@coursemail.umd.edu, chem433-0101-spr19@coursemail.ur **2 more**
Bcc Ross Salawitch

Hi Everyone,

Hope you had an enjoyable winter break. I am using the UMEG generated alias to welcome folks enrolled in AOSC / CHEM 433 & AOSC 633, Atmospheric Chemistry and Climate, which will start on Tues, Jan 28, at 2 pm in room 2416 of the Atlantic Building (bldg #224 on campus maps).

I am writing simply to welcome folks and let you know:

a) I will maintain my own website for the class at:

http://www.atmos.umd.edu/~rjs/class/spr2019 that will also be tied into the ELMS page https://umd.instructure.com/courses/1256337

b) we will be using the 7th Edition of Chemistry in Context by ACS as the *required text* for the class because this "N-1" version of this manuscript, which I helped write, is available *used* at *very low cost* from a variety of sellers and, most importantly, **can also be rented from me for $20 that will be returned at the end of the semester (upon return of the book).**

c) we will also be using readings from other books that will be provided electronically.

If you fell compelled to permanently keep all of your textbooks, you are welcome to acquire Chemistry in Context:

https://www.amazon.com/gp/offer-listing/0073375667/ref=sr_1_5_olp?ie=UTF8&qid=1548639690&sr=8-5&keywords=chemistry+in+context

If so, please be sure to get the 7th edition, as I'll assign section numbers that change from edition to edition. I have plenty of copies, enough for everyone to rent from me for a fully refundable $20 fee, upon return of the book at the end of the semester. Will bring the stack of books to the first class. If you are "course shopping" and not sure you'll stay in the class, can wait until Thurs to rent the book, since the first reading from this book will be for our Tues, 5 Feb meeting. If you're sure you'll stick with the class, great if you can try to have $20 available on

All class related, group emails will be logged at

http://groups.google.com/group/atmospheric-chemistry-and-climate-2019

for any and all to see !

Organization Details

- Admission Tickets (AT) (20%)
  - short set of questions, related to lecture; *completed prior to the start of each class*
  - posted on web page; straightforward if reading has been done
  - graded on a 10 point basis; *lowest three scores will be dropped*
  - please complete on ELMS and email me and Walt if you are having a problem with ELMS
- Problem Sets (30%)
  - posted on web page and announced in class at least 1 week before due date
  - assignment about every two to three weeks; 6 total
  - prescribed "late penalty" and final receipt date: will not be accepted after solutions have been handed out (typically within ~7 days of due date)
  - problem sets are new each year; access to old solutions will be of little or no benefit
- Exams (50%)
  - two in-class exams (early semester; late semester) plus final exam, same weights
  - exams will tend strongly towards understanding of concepts via essay-like answers whereas problem sets will tend strongly towards quantitative understanding
- Prerequisite
  - CHEM131, CHEM135, or CHEM146 plus MATH241 or permission of CMNS-Atmospheric & Oceanic Science department
  - Class will be taught at a level accessible to any upper level (JR or SR) physical science major (i.e., adept at use of equations; has seen a differential, an exponential, understands the basic concept of integration, etc)

Organization Details

- Students enrolled in 633:
  - 6 to 8 page, single-spaced (not including references and figures) **research paper** plus a **verbal presentation** on same topic
  - ***paper/presentation will contribute to final grade in an amount equal to each exam***
  - extra question on some problem sets
  - a few different questions on exams (some overlap)
- Grading:
  - admission tickets: 20%
  - problem sets: 30%
  - in-class exam I and II: 16.67% each (closed book; no notes)
  - final exam: 16.67% (closed book; no notes)
  - collaboration policy posted on class website: problems sets & admission tickets should reflect your own work & understanding of the material
- Office hours:
  - Ross (ATL 2403) : Mon, 2:00 to 3:00 pm
  - Walt (ATL 4100): By arrangement
  - We strive to be accessible throughout the semester. Please either drop by (one of us is usually around) or contact us via email to set up a time to meet
  - Finally: *Ross is generally quite busy just before class*; would be great if you would strive to seek assistance from Walt if you need help within ~30 min of class

Organization Details, Continued

- Readings
  - All readings, except those from required text, will be posted on class webpage
  - Handouts of selected readings will be provided
  - Publicly available PDF files will be "unprotected"
  - Copyright protected PDF files will be protected, using **password given out in class**
- Additional Readings
  - Provided for many lectures for students who would like more in depth info, to enhance learning experience for motivated students
  - If noted with an asterisk additional reading is "strongly suggested" for students enrolled in 633; could be used for a question on 633 problem set or exam
- Email
  - ***Please use AOSC 433, CHEM 433, or AOSC 633 at start of subject line of class-related email and please send emails to me and Walt***

Electronic devices:

Cell phones on mute

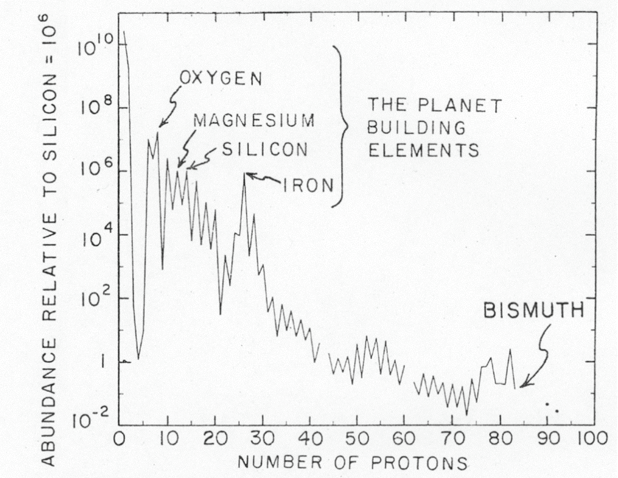
Use laptop or iPad for taking notes is fine

Use of laptop, iPad, or cell phone for non-class purpose prohibited without prior arrangement

---

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**

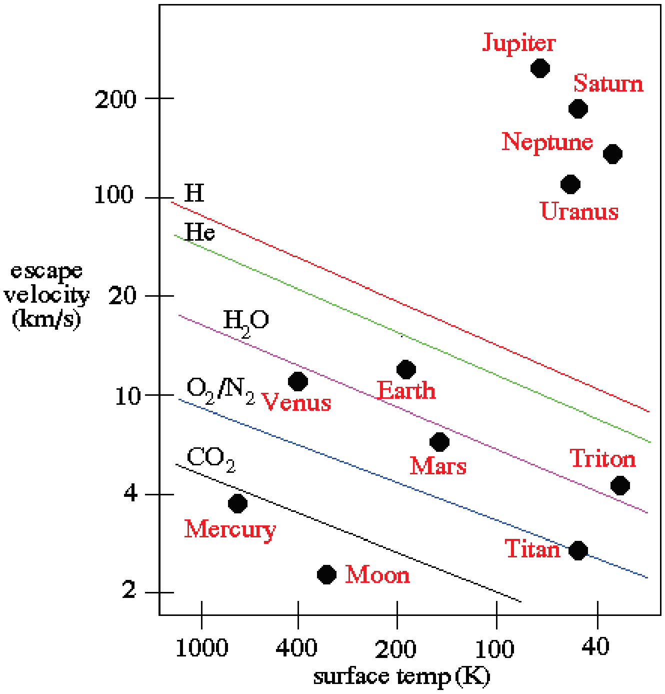


From "How to Build a Habitable Planet"
By W.S. Broecker, ELDIGIO Press, pg 57

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

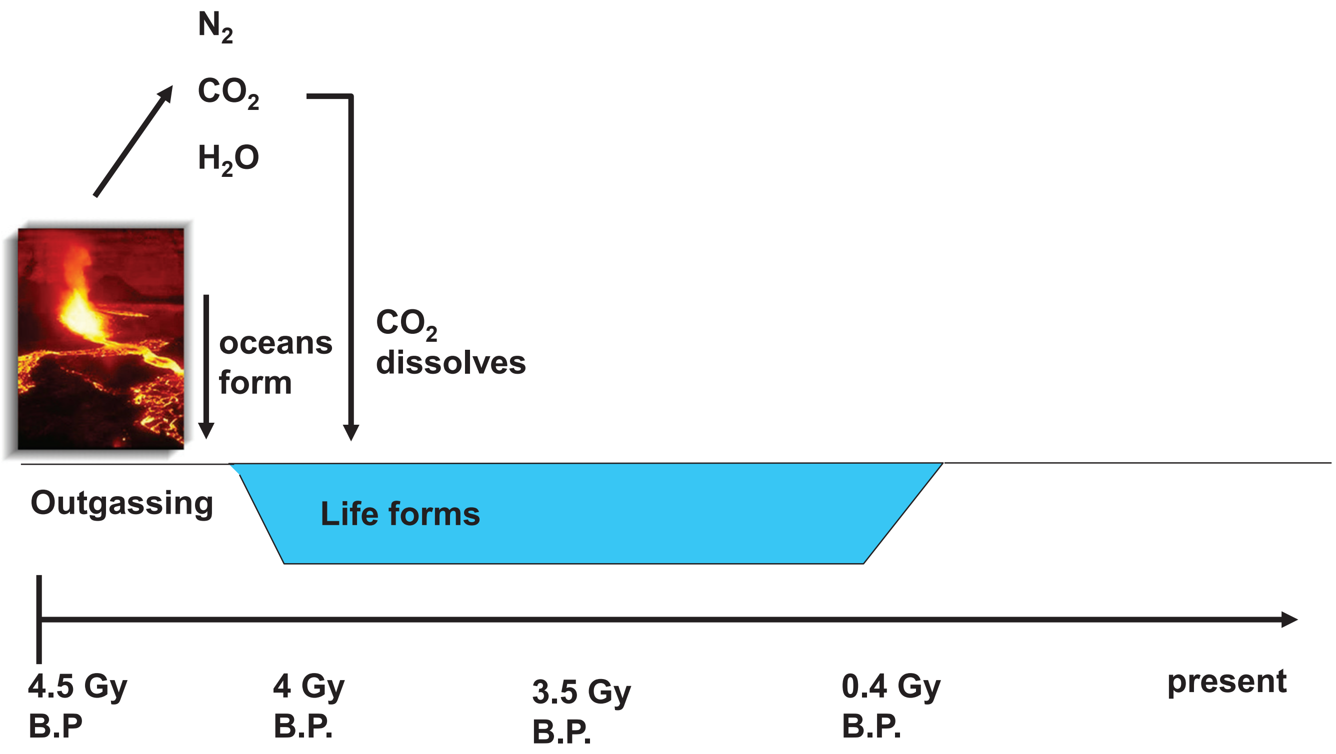
	Earth	Venus	Mars
Radius (km)	6400	6100	3400
Mass (10^{24} kg)	6.0	4.9	0.6
Albedo	0.3	0.8	0.22
Distance from Sun (A.U.)	1	0.72	1.52
Surface Pressure (atm)	1	91	0.007
Surface Temperature (K)	~15 °C	~ 460 °C	–140 °C to 20 °C
N_2 (mol/mol)	0.78	3.4×10^{-2}	2.7×10^{-2}
O_2 (mol/mol)	0.21	6.9×10^{-5}	1.3×10^{-3}
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:
Outgassing



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: $\sum = -2 \times \#\text{ O atoms} + 1 \times \#\text{ H atoms}$;
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

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

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

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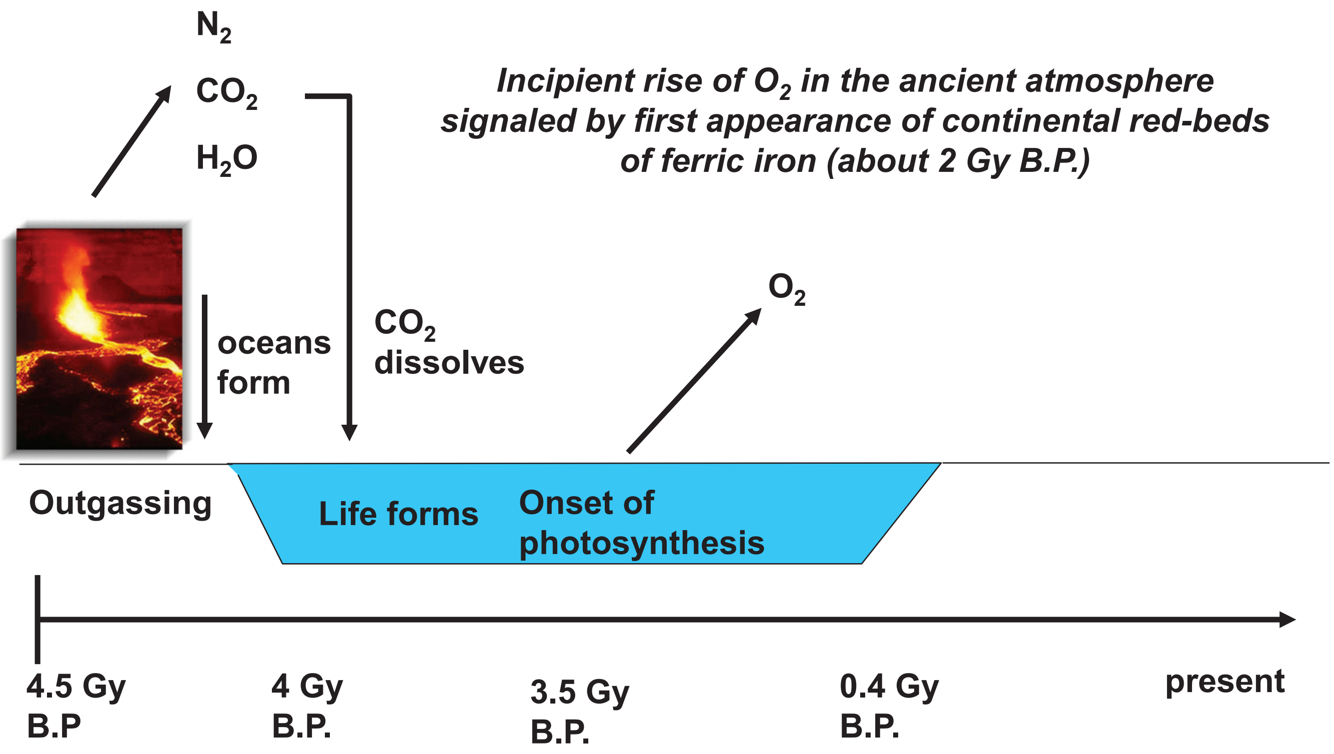
Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Reducing Environment

How do we know early atmosphere was reducing ?

Why was a reducing environment important ?

Geological Evolution of Earth’s Atmosphere:
Onset of Photosynthesis

Incipient rise of O_2 in the ancient atmosphere signaled by first appearance of continental red-beds of ferric iron (about 2 Gy B.P.)



N_2

CO_2

H_2O

oceans form

CO_2 dissolves

O_2

Outgassing

Life forms

Onset of photosynthesis

4.5 Gy B.P

4 Gy B.P.

3.5 Gy B.P.

0.4 Gy B.P.

present

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:**

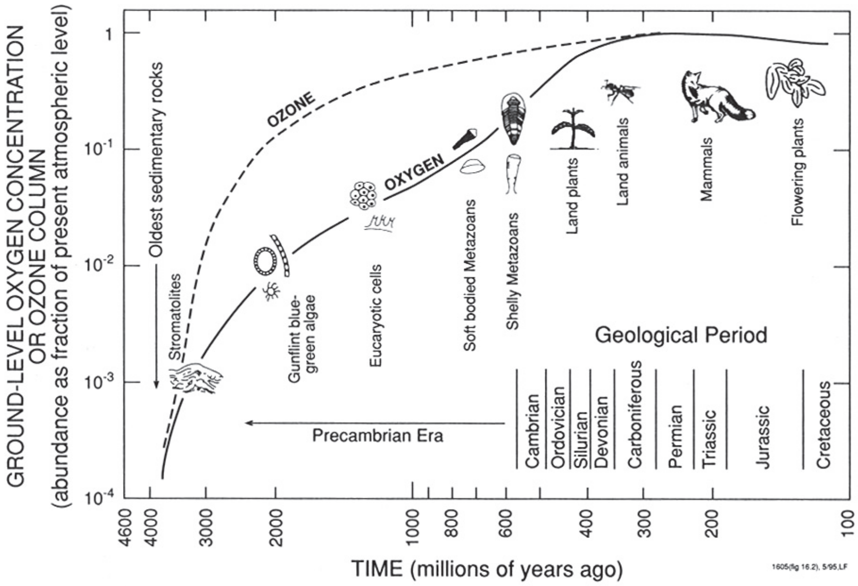


Figure 16.3. *Probable evolution of the oxygen and ozone abundance in the atmosphere (fraction of present levels) during the different geological periods of the Earth’s history (Wayne, 1991; reprinted by permission of Oxford University Press).*

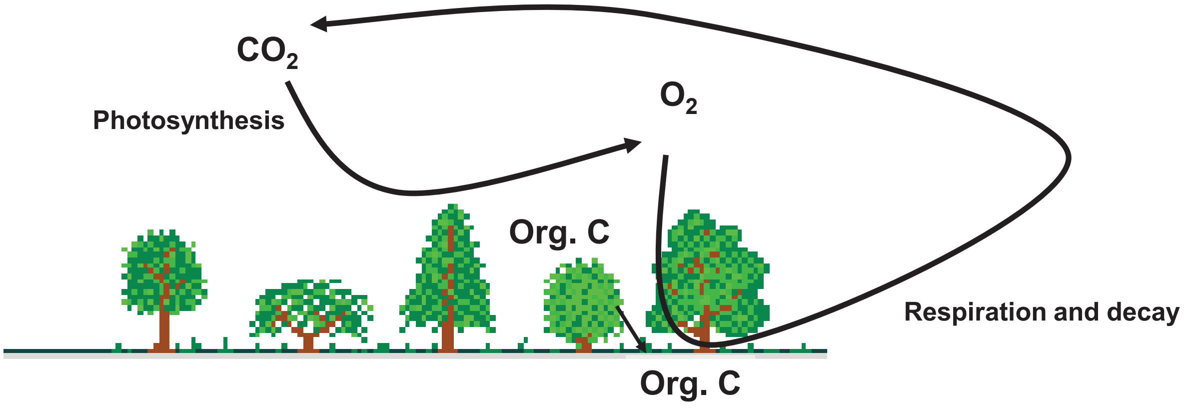
Geological Evolution of Earth’s Atmosphere:
Early Atmosphere: Photosynthesis

- **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**

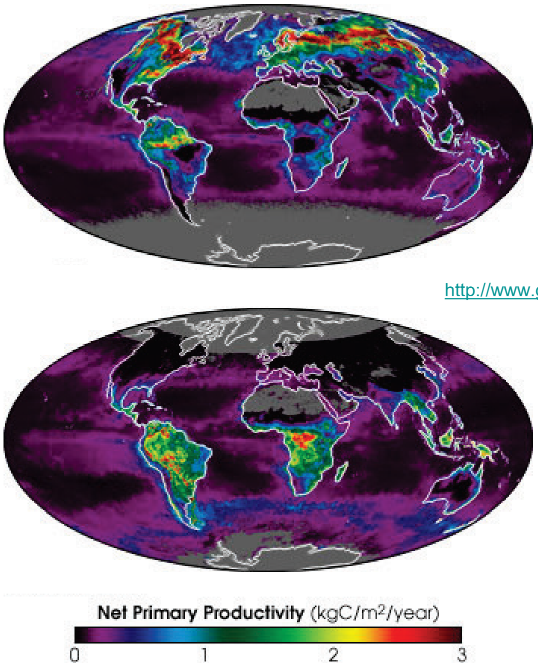
$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$



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

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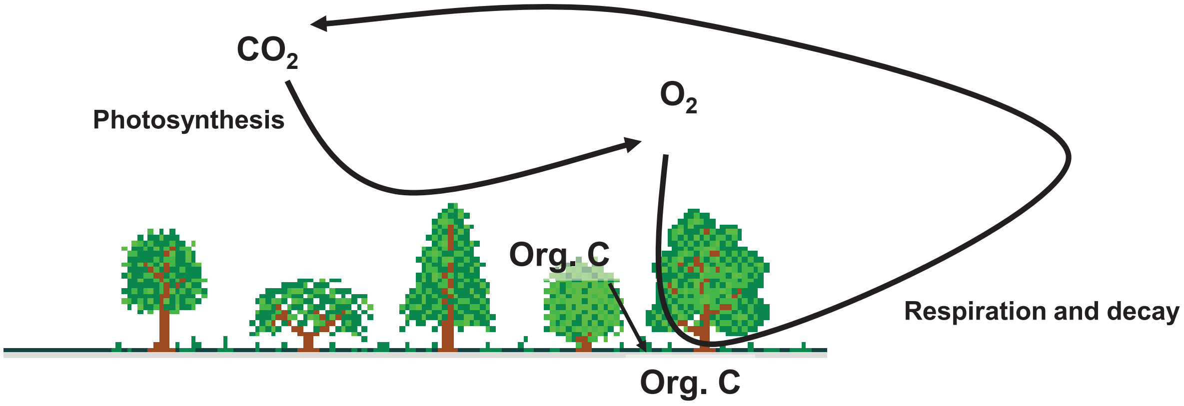
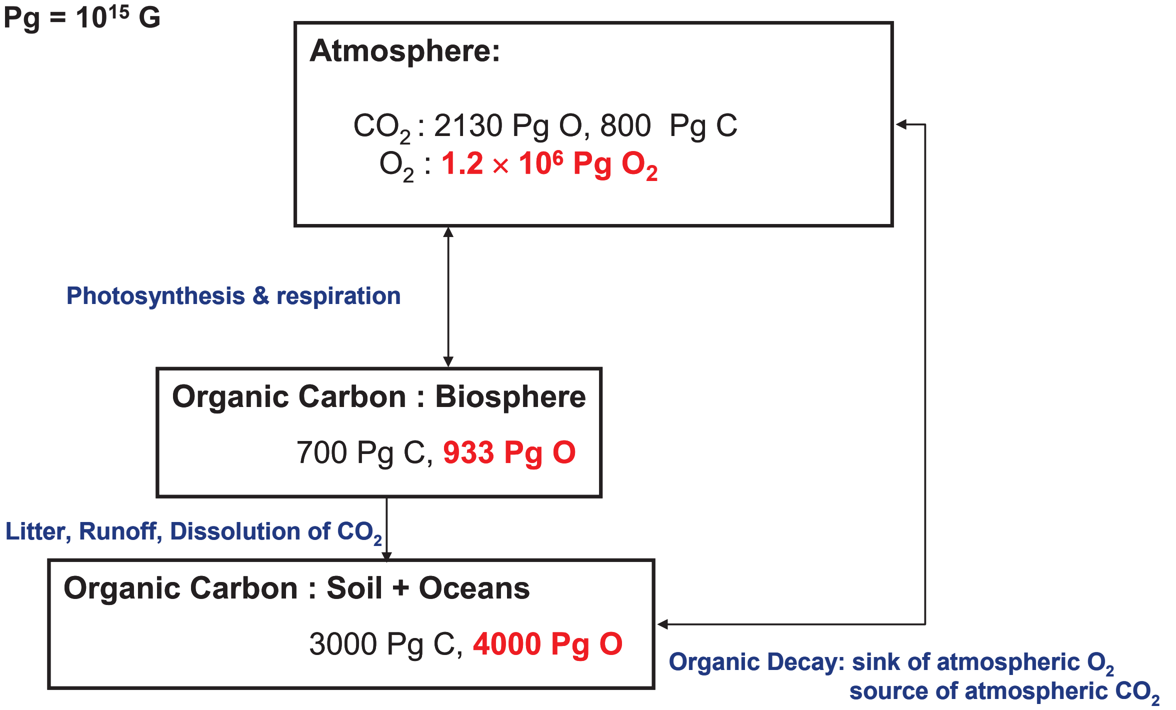
Geological Evolution of Earth’s Atmosphere:
Early Atmosphere: Photosynthesis

- **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}
  Production of atmospheric O_2 is therefore ~152×10^{15} g O_2 yr^{-1}
- **Mass O_2 in atmosphere = $0.21 \times (5.2 \times 10^{21}$ g$) \times (32 / 29) \approx 1.2 \times 10^{21}$ g**
- **Lifetime of atmospheric O_2 due to biology = 1.2×10^{21} g / (152×10^{15} g O_2 yr^{-1})**



Geological Evolution of Earth’s Atmosphere:
Oxygen and Carbon Reservoirs

1 Pg = 10^{15} G



Atmosphere:

CO_2 : 2130 Pg O, 800 Pg C
O_2 : **1.2×10^6 Pg O_2**

Photosynthesis & respiration

Organic Carbon : Biosphere

700 Pg C, **933 Pg O**

Litter, Runoff, Dissolution of CO_2

Organic Carbon : Soil + Oceans

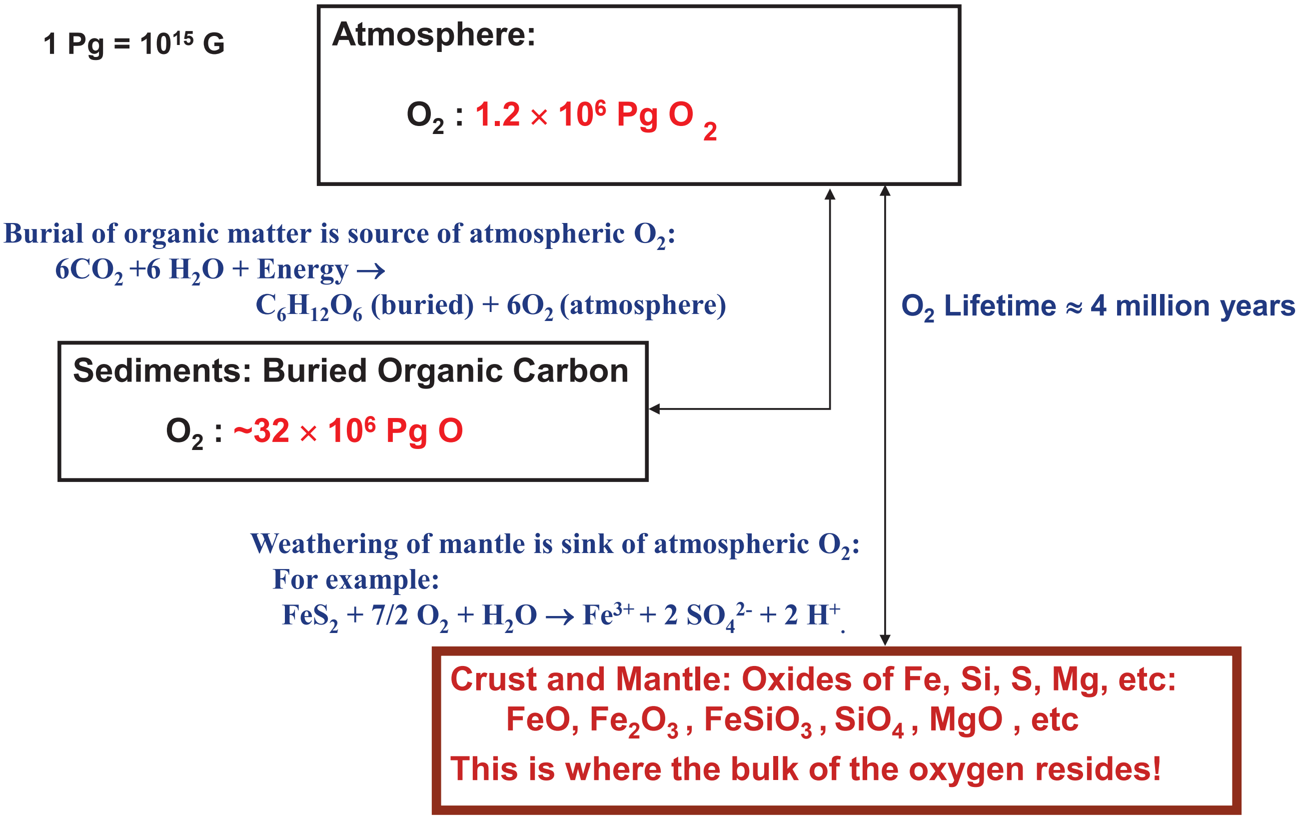
3000 Pg C, **4000 Pg O**

Organic Decay: sink of atmospheric O_2
source of atmospheric CO_2

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

O_2 Lifetime ≈ 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

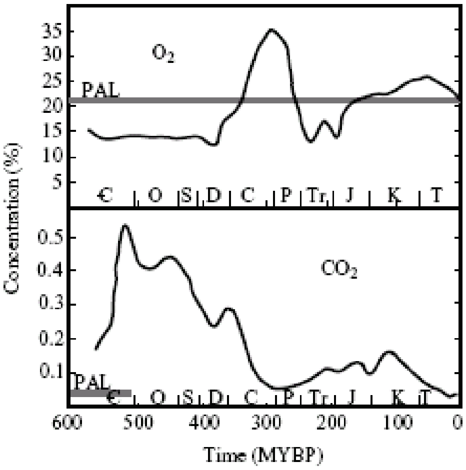
- **Rise of atmospheric O_2 linked to evolution of life:**
  - **400 My B.P. O_2 high enough to form an ozone layer**
  - **400 to 300 My B.P.: first air breathing lung fish & primitive amphibians**

- **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

~500 to 300 My B.P.

- **Development of vascular land plants**
- **Plants became bigger and bigger and less reliant on water**
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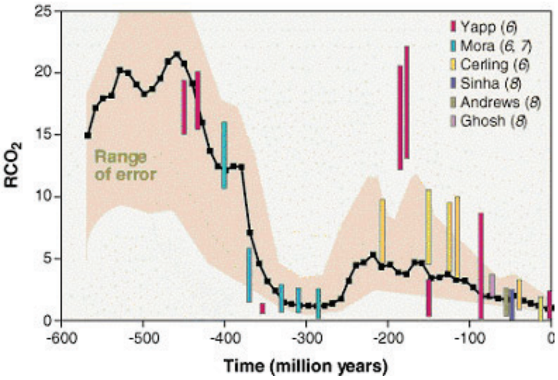
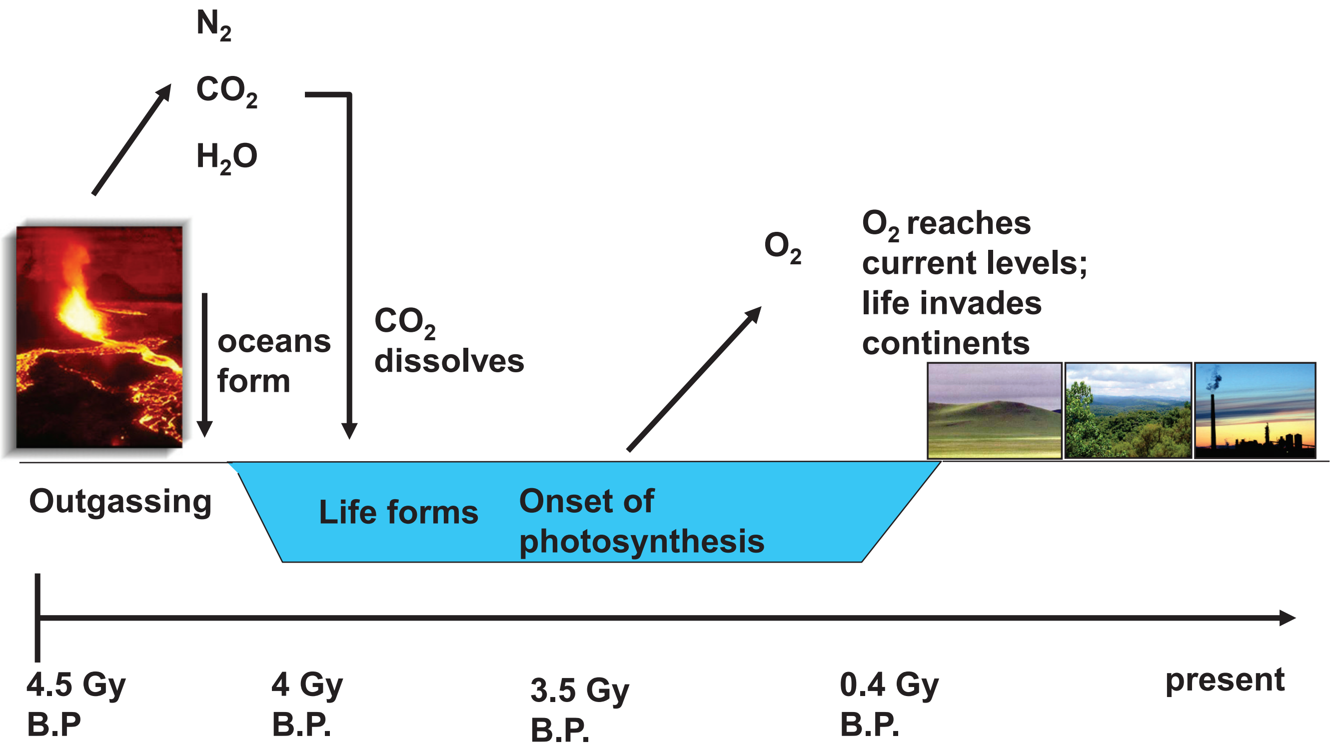


From R. Berner, *Science,* 276, 544, 1997.

Geological Evolution of Earth’s Atmosphere:
Human Influence



N_2

CO_2

H_2O

oceans form

CO_2 dissolves

O_2

O_2 reaches current levels; life invades continents

Outgassing

Life forms

Onset of photosynthesis

4.5 Gy B.P

4 Gy B.P.

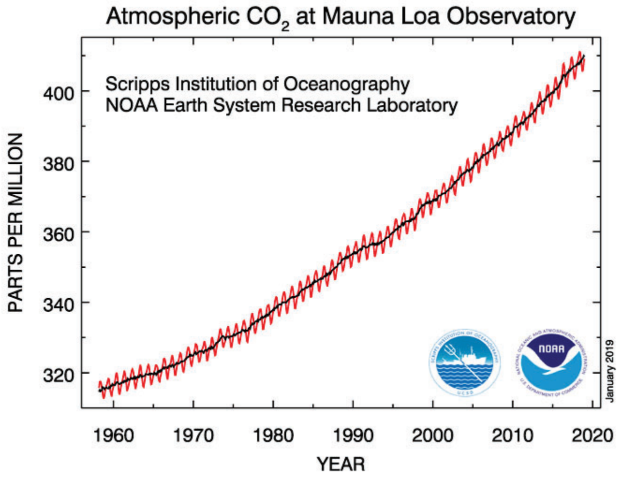
3.5 Gy B.P.

0.4 Gy B.P.

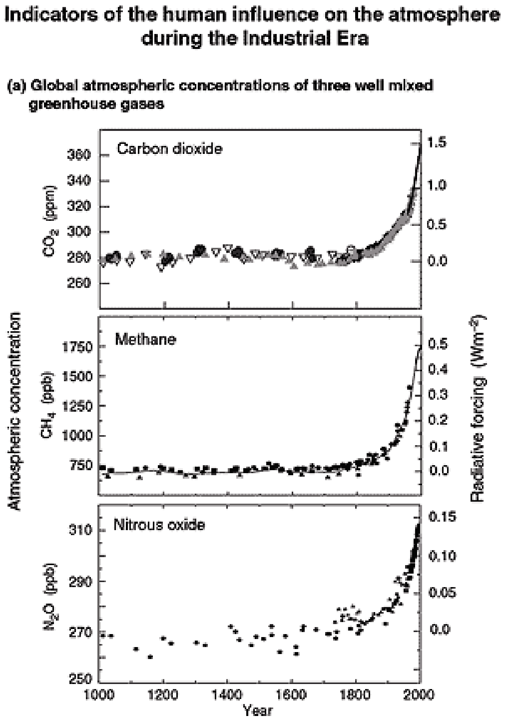
present

Earth’s Atmosphere – Effect of Humans

CO_2: ~398 parts per million (ppm) and rising !



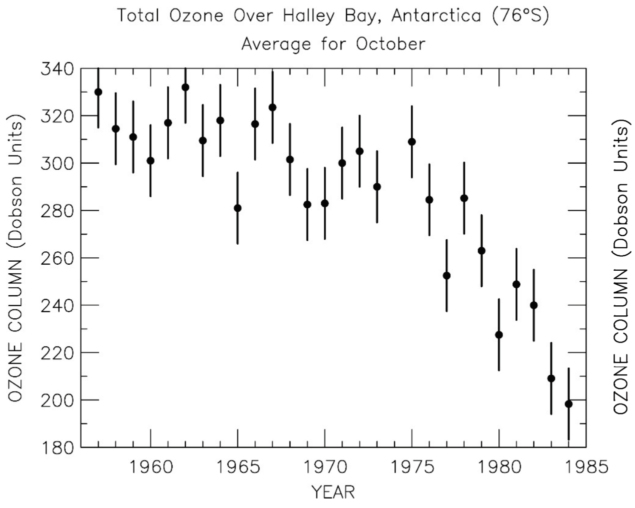
Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
https://www.esrl.noaa.gov/gmd/ccgg/trends/full.html



Climate Change 2001: IPCC Synthesis Report
http://www.grida.no/climate/ipcc_tar/vol4/english/index.htm

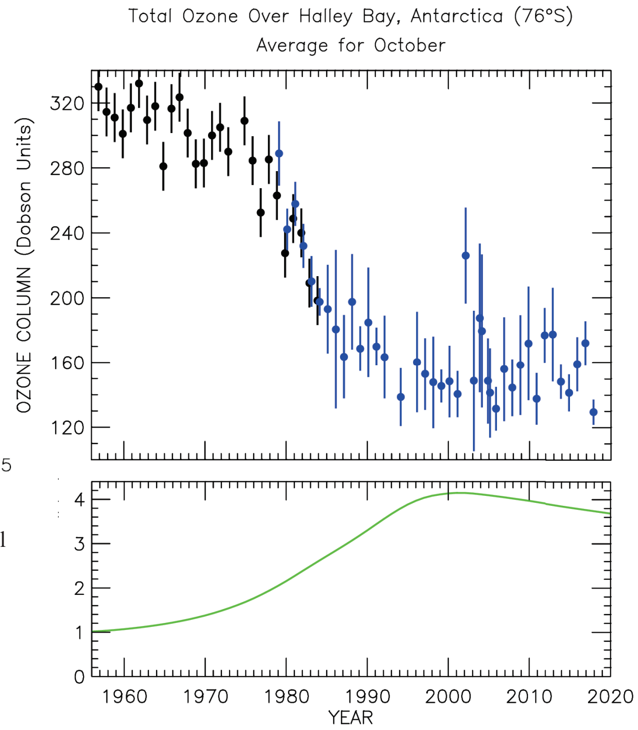
Earth’s Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation

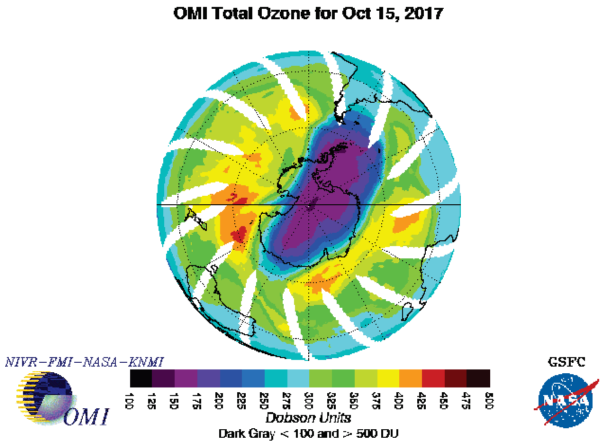


After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.

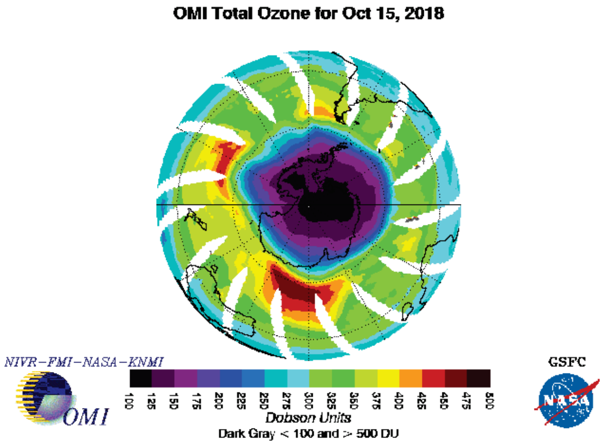
Update



Earth’s Atmosphere – Effect of Humans



ftp://toms.gsfc.nasa.gov/pub/omi/images/spole/Y2017/



ftp://toms.gsfc.nasa.gov/pub/omi/images/spole/Y2018/

Earth’s Atmosphere – Effect of Humans

Tropospheric Ozone – oxidant, lung irritant, harmful to crops

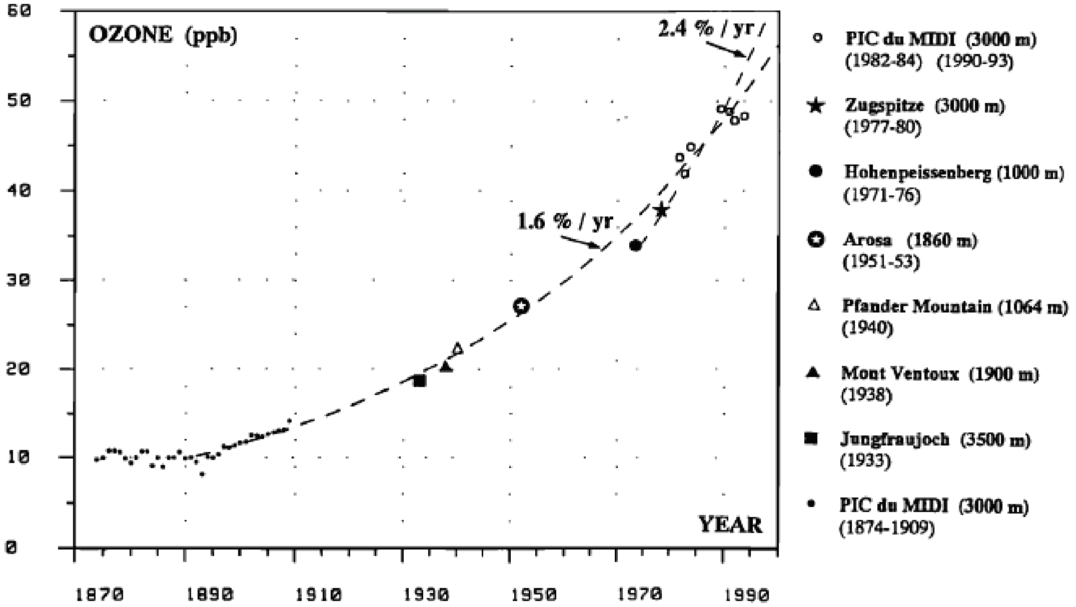
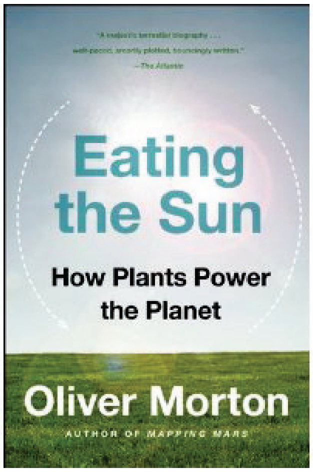


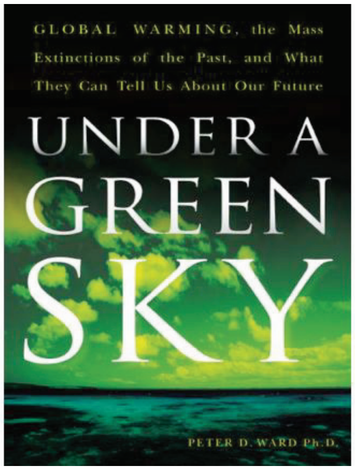
Figure 5. Ozone evolution in the free atmosphere over western Europe, from measurements at the Pic du Midi and in various European stations at high altitudes (see text).

Marenco *et al.*, *JGR*, 1994

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 source material for much of this lecture

Next Lecture: Course Overview

Readings: IPCC 2007 FAQ 1.1, 1.2, 1.3, 2.1, & 3.1 (11 pages)
EPA Air Quality Guide (11 pages)
WMO Ozone FAQ 1, 2, 3, 8,15 (12 pages)
Paris Beacon of Hope, Sect 1.2.2 (3 pages)
Note: 37 pages, about our norm

Admission Ticket for Lecture 2 is posted on ELMS