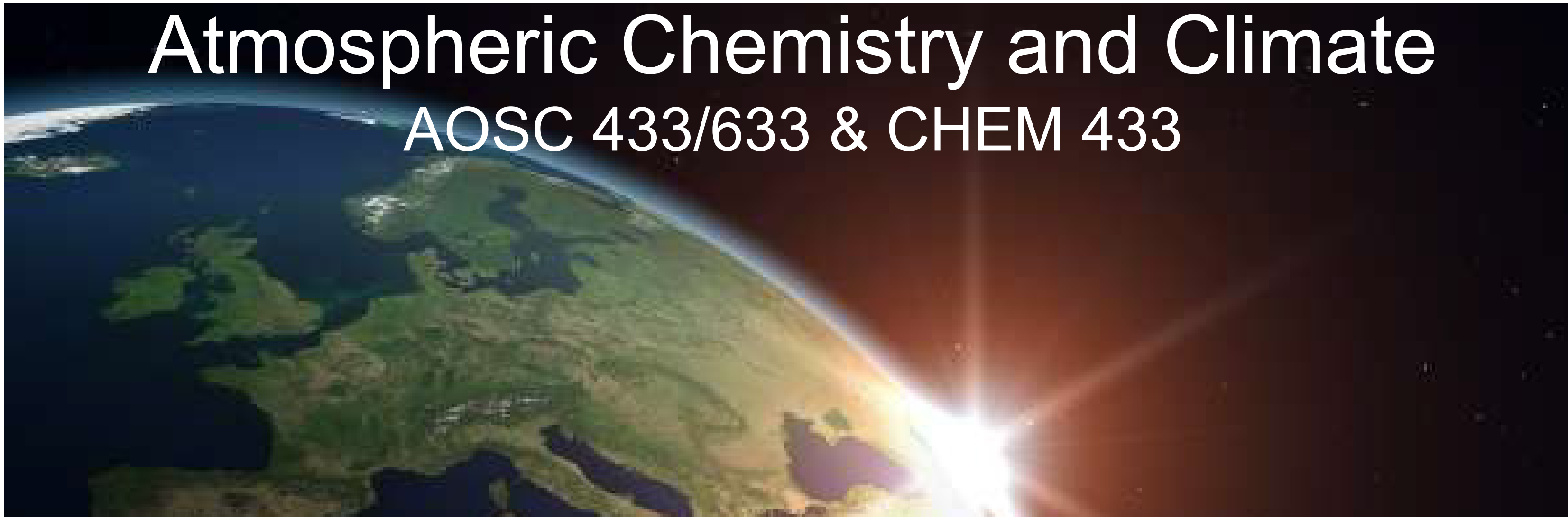
Atmospheric Chemistry and Climate

AOSC 433/633 & CHEM 433



Ross Salawitch (rjs@atmos.umd.edu): Professor

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Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

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

Supplemental Texts:

Global Warming: The Complete Briefing 3d Edition by John Houghton

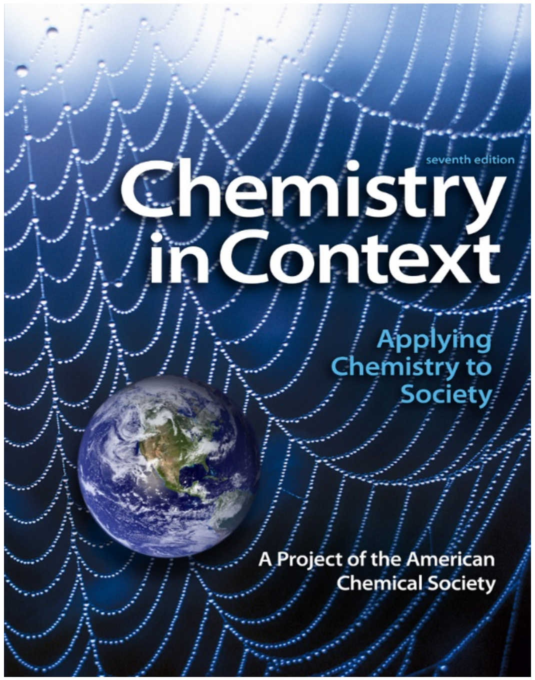
The Atmospheric Environment by Michael B. McElroy

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

Lecture 1

27 January 2015

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
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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

- Fairly active used book market for 7th edition, since the Jan 2014 release of 8th edition
- Changes from edition to edition are minor: we will use 7th edition to save you $$$
- Available for rent from me, for $20, refundable at end of semester upon return of book
- Not have enough rentable books for entire class; some of you will likely want to keep the book after end of the semester. If so, please purchase 7th edition on line rather than rent from me
- We'll hand out copies of early readings from this book, but will stop at a certain point

Class Website

2. Schedule

Date	Lecture Topic	Required Reading	Admis. Tickets	Lecture Notes	Learning Outcome	Problem Sets*	Additional Readings
01/27	Geological Evolution of Earth's Atmosphere	NY Times article (teaching philosophy)		Lecture 1 √ Video	Quiz		
01/29	Overview of Global Warming, Air Quality, & Ozone Depletion	IPCC 2007 FAQ (questions 1.1, 1.2, 1.3, 2.1, & 3.1) EPA AQI Brochure (entire document; only 11 pgs) WMO 2010 20 QAs (questions 1, 2, 3, 10, 15 & 18) Click here for entire WMO 2010 QAs Click here for entire IPCC 2007 FAQ	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
02/03	Fundamentals of Earth's Atmosphere	Chemistry in Context: Secs 1.0 to 1.2, 1.5 to 1.8, 1.14, 2.1, & 3.6 to 3.7 (~28 pgs)	AT 3 ×	Lecture 3 × Video	Quiz		Houghton, Ch 2

http://www.atmos.umd.edu/~rjs/class/spr2015

Organization Details

- Admission Tickets (AT) (10%)
  - short set of questions, related to lecture; *turned in at 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*
  - can send completed admission ticket prior to class via either email
- Group Quizzes (GQ) (5%)
  - students will break into small groups, 4 students max, each led by a student enrolled in AOSC 633/0101, *during class*
  - group will provide single answer to assigned question with a strict 5 min time limit
  - answer will be reviewed either in class that day –or– start of next lecture
  - graded on a 10 point basis; *lowest two scores will be dropped*
  - students with an excused absence will receive mean of that day's GQ whereas unexcused absence will result in score of 0 for that GQ
- Problem Sets (25%)
  - 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 (60%)
  - 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

Organization Details

- Students enrolled in 633/0101 & 633/AM01:
  - 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 equal to each exam
  - extra question on most problem sets
  - different questions on exams (some overlap)
- Grading:
  - admission tickets: 10%
  - group quizzes: 5%
  - problem sets: 25%
  - in-class exam I and II: 20% each (closed book; no notes)
  - final exam: 20% (closed book; no notes)
  - collaboration policy posted on class website: problems sets & admission tickets should reflect your own work & understanding of the material, whereas the in-class group quizzes will hopefully reflect input from all participants
- Office hours:
  - Ross (CSS 2403) : Mon, 2:00 to 3:00 pm
  - Austin (CSS 4365): Mon, 3:00 to 4:00 pm & Wed, 2:00 to 3:00 pm
  - Tim (CHE bldg 090, Room1305): Wed, 3:00 to 4:00 pm
  - 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 please strive to seek assistance from TAs if you need help within ~30 min of lecture

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 Austin***

Electronic devices:

Cell phones on mute

Use laptop or iPad for taking notes is fine

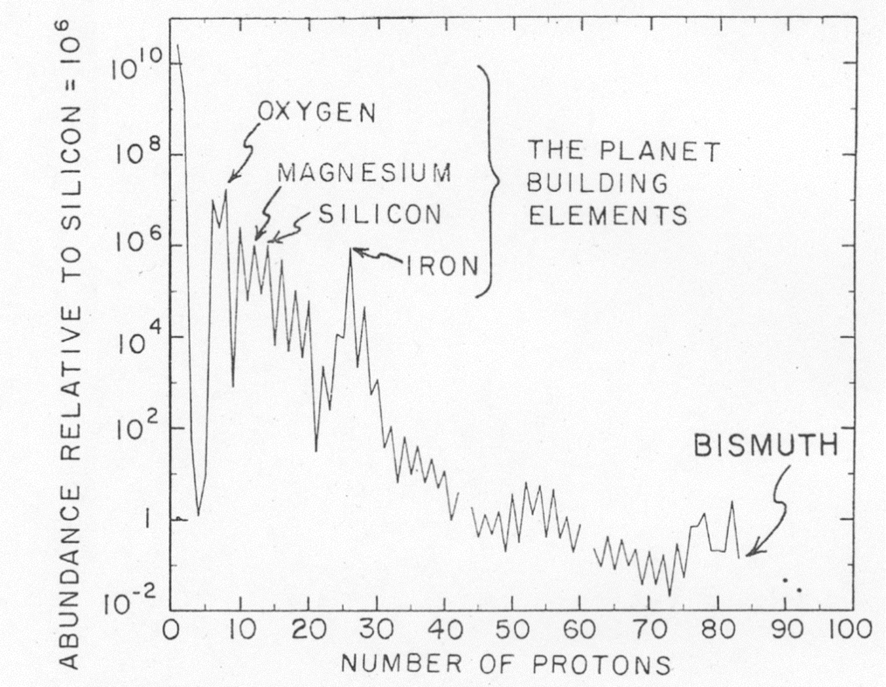
Use of laptop, iPad, or cell phone for non-class purpose prohibited without prior arrangement

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**

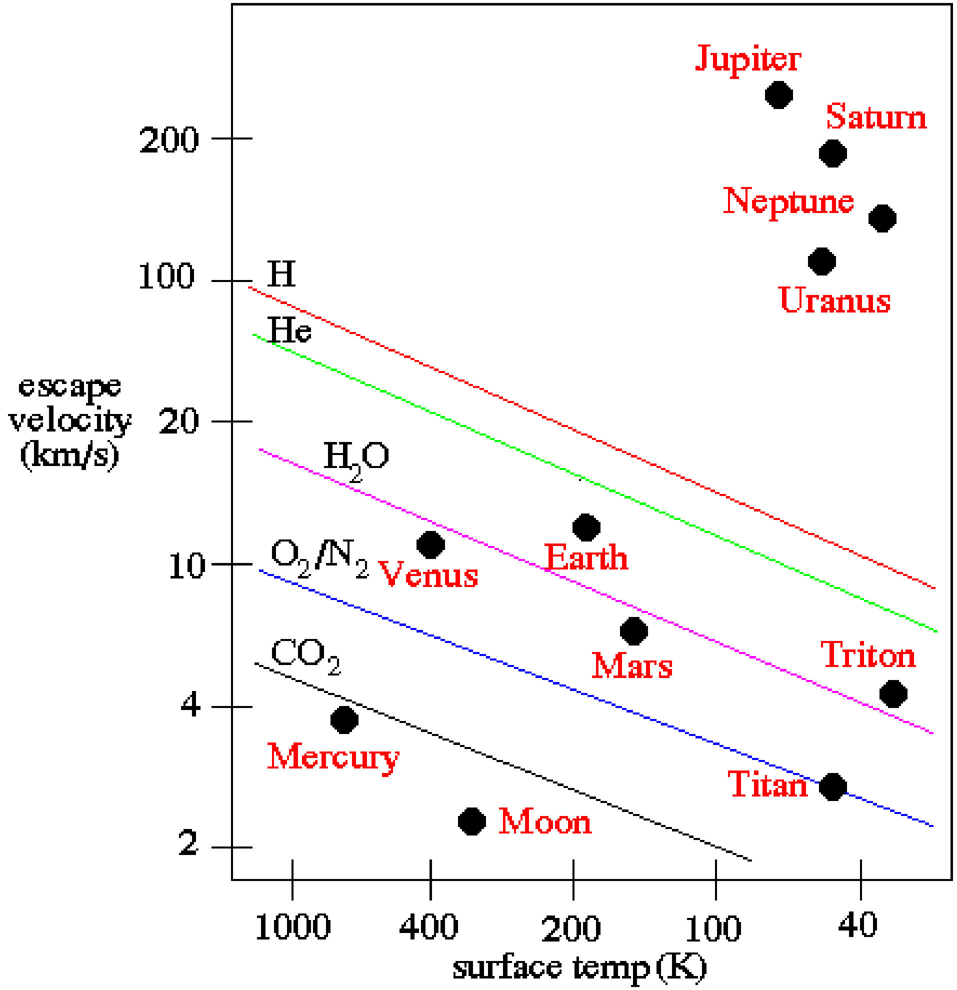


From "How to Build a Habitable Planet"
By W.S. Broecker, ELDIGIO Press, pg 57

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

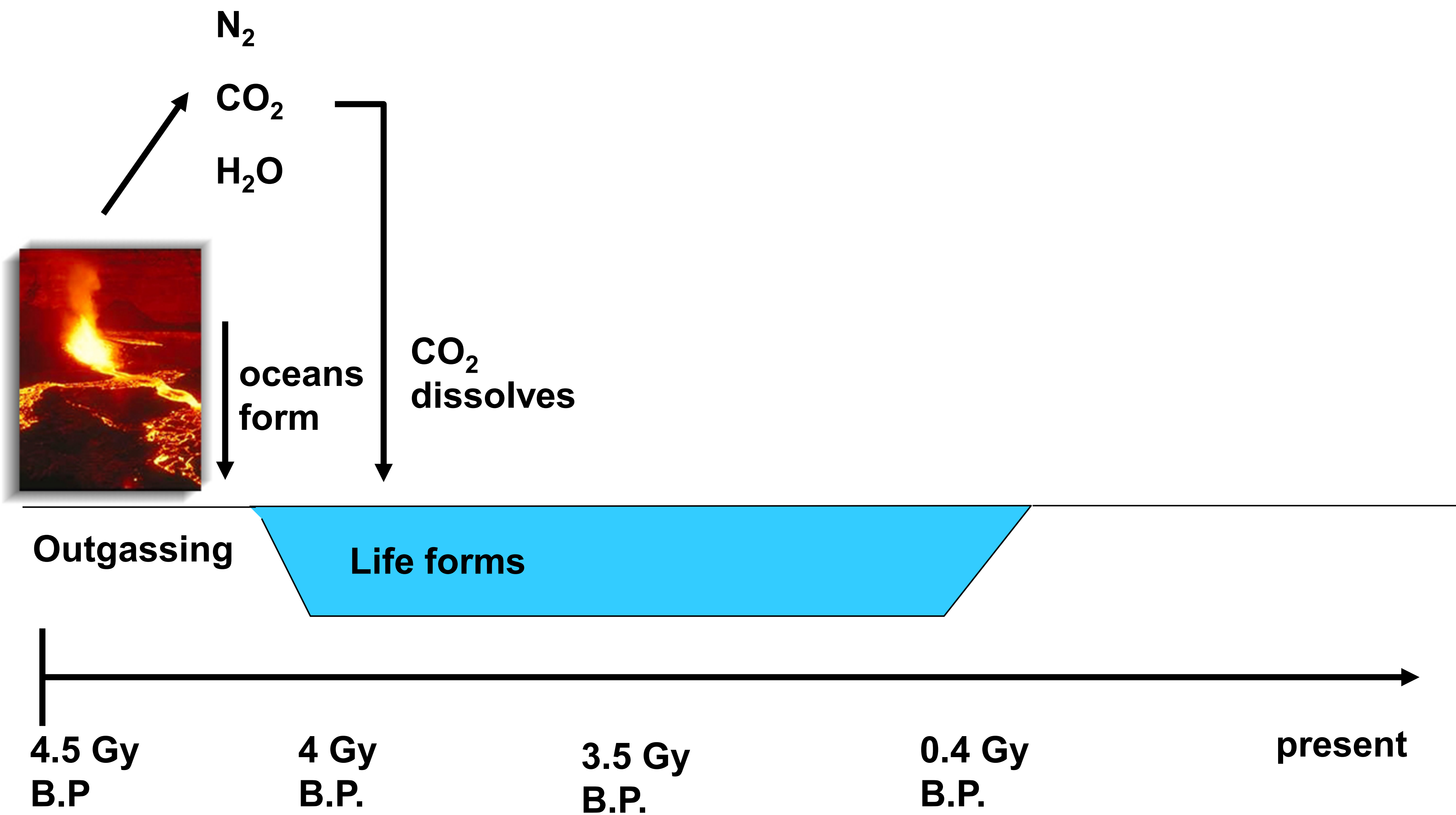
	Earth	Venus	Mars
Radius (km)	6400	6100	3400
Albedo	0.3	0.8	0.22
Distance from Sun (A.U.)	1	0.72	1.52
Surface Pressure (atm)	1	91	0.007
Surface Temperature (K)	~15 °C	~ 460 °C	–140 °C to 20 °C
N_2 (mol/mol)	0.78	3.4×10^{-2}	2.7×10^{-2}
O_2 (mol/mol)	0.21	6.9×10^{-5}	1.3×10^{-3}
CO_2 (mol/mol)	3.7×10^{-4}	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: $\sum = -2 \times \#$ 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:
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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

N_2

CO_2

H_2O

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.)

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 Dorian 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 ?!?

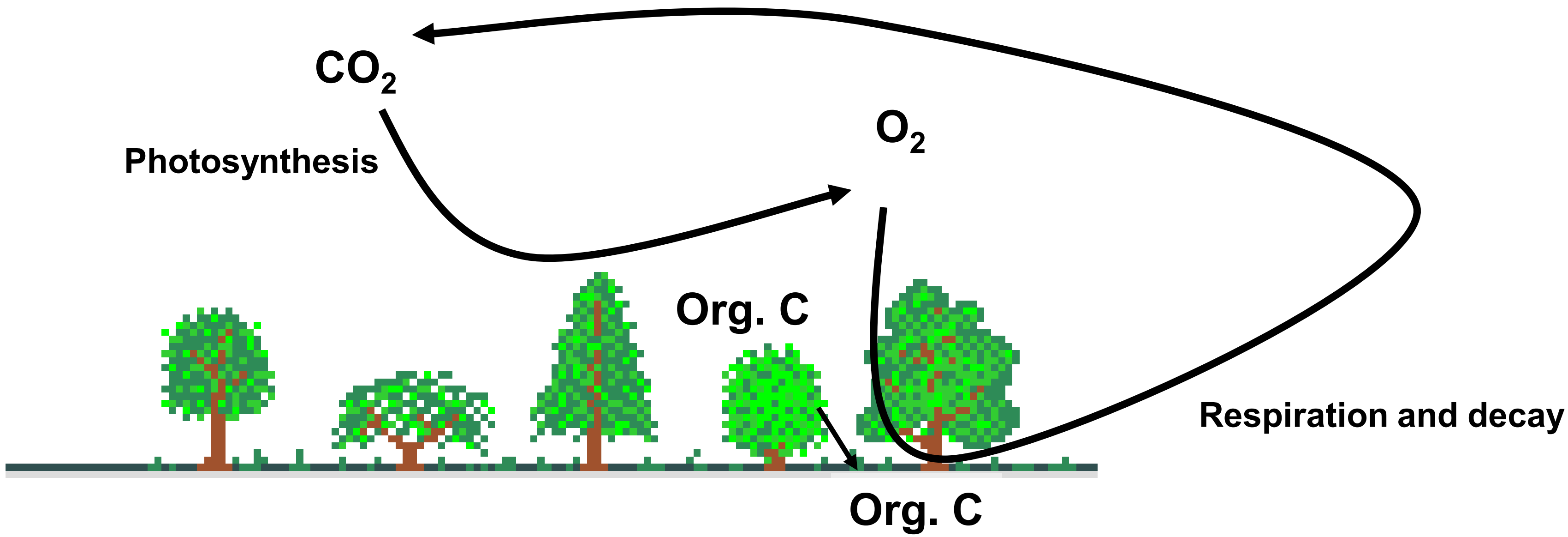
Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

- **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**

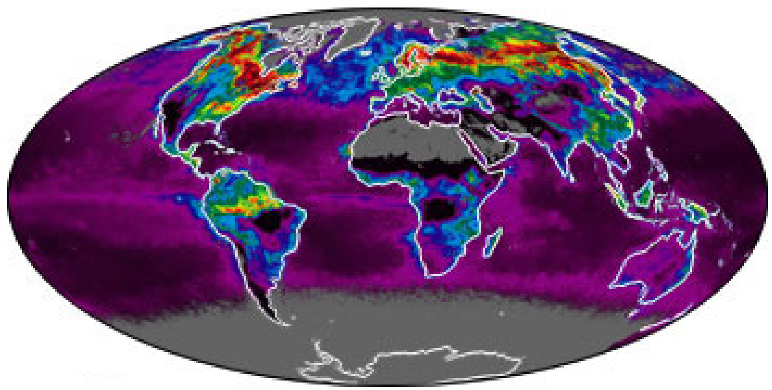
$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$



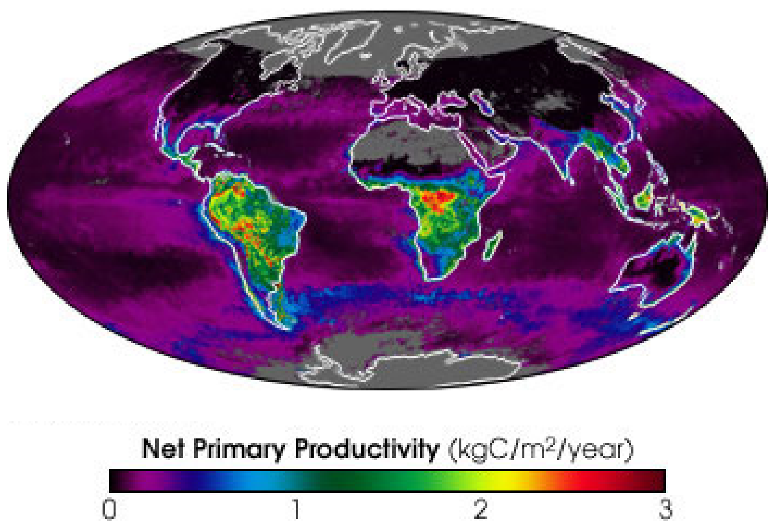
Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

- **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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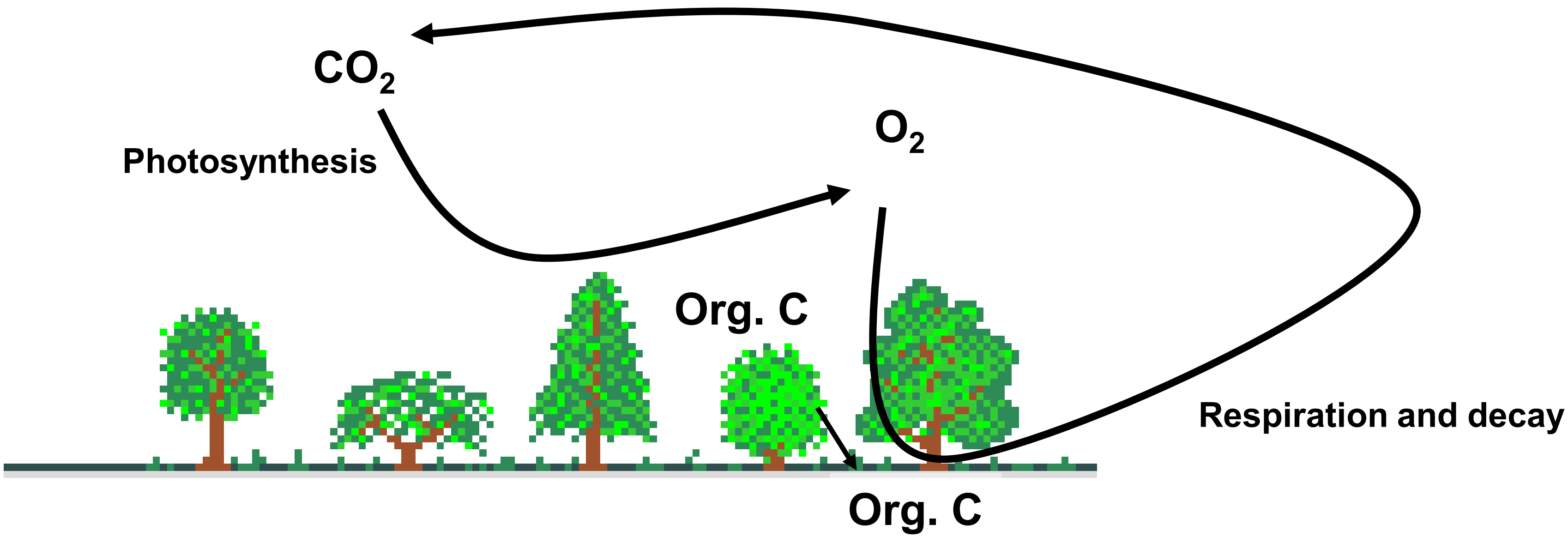
  $6\ CO_2 + 6\ H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\ O_2$ is ~ 57×10^{15} g C yr^{-1}
  Production of atmospheric O_2 is therefore ~152×10^{15} g O_2 yr^{-1}

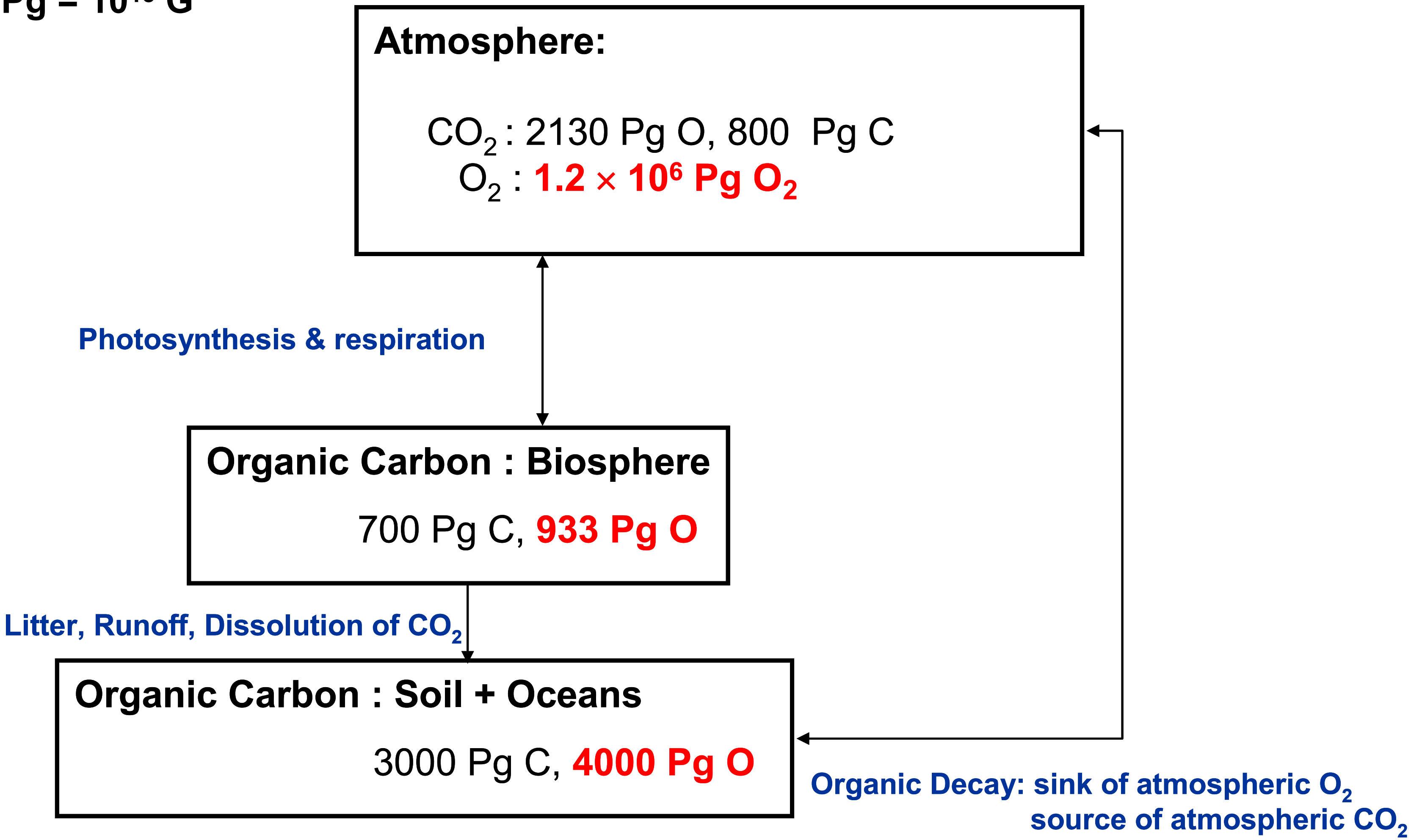
- **Mass O_2 in atmosphere = $0.21 \times (5.2 \times 10^{21}$ g$) \times (32 / 29) \approx 1.2 \times 10^{21}$ g**

- **Lifetime of atmospheric O_2 due to biology = 1.2×10^{21} g / (152×10^{15} g O_2 yr^{-1})**
  $\approx$ 8,000 yr



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:

$6CO_2 + 6\,H_2O + \text{Energy} \rightarrow$

$C_6H_{12}O_6$ (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:**

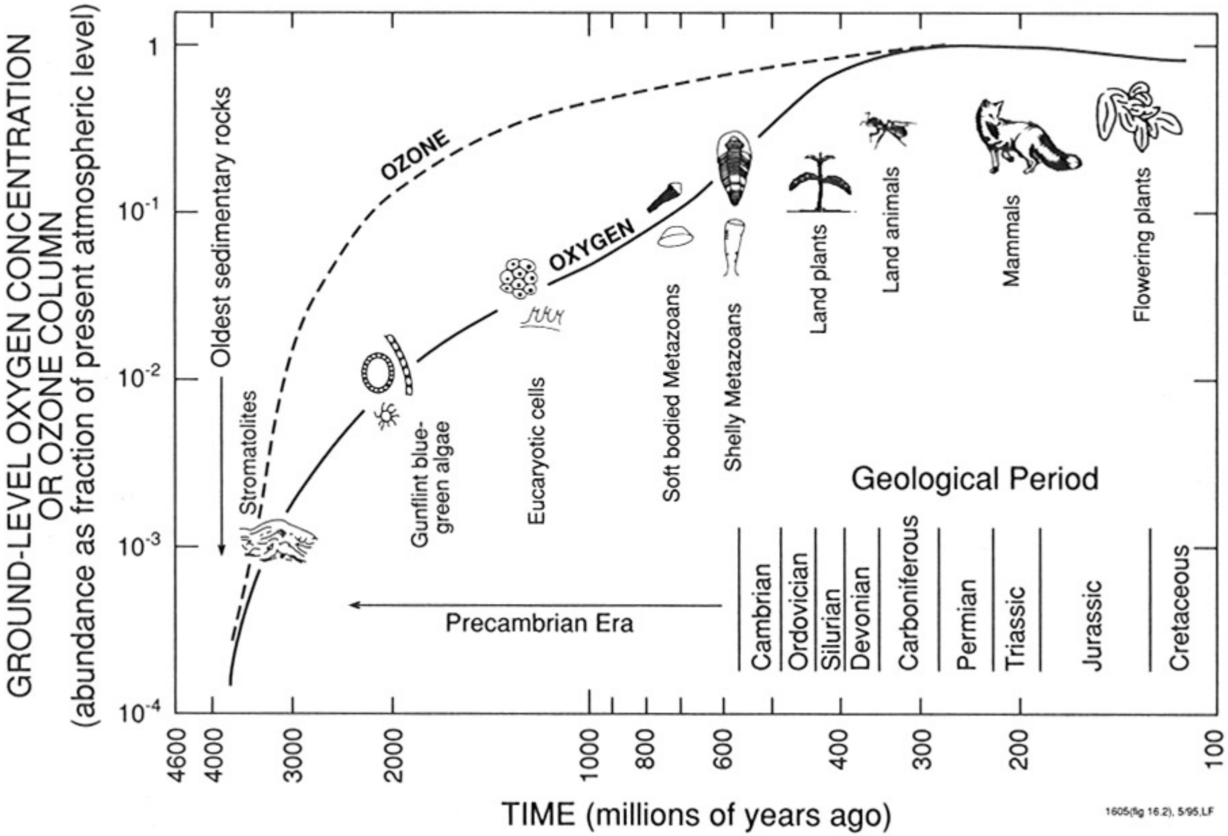


Figure 16.3. *Probable evolution of the oxygen and ozone abundance in the atmosphere (fraction of present levels) during the different geological periods of the Earth's history (Wayne, 1991; reprinted by permission of Oxford University Press).*

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

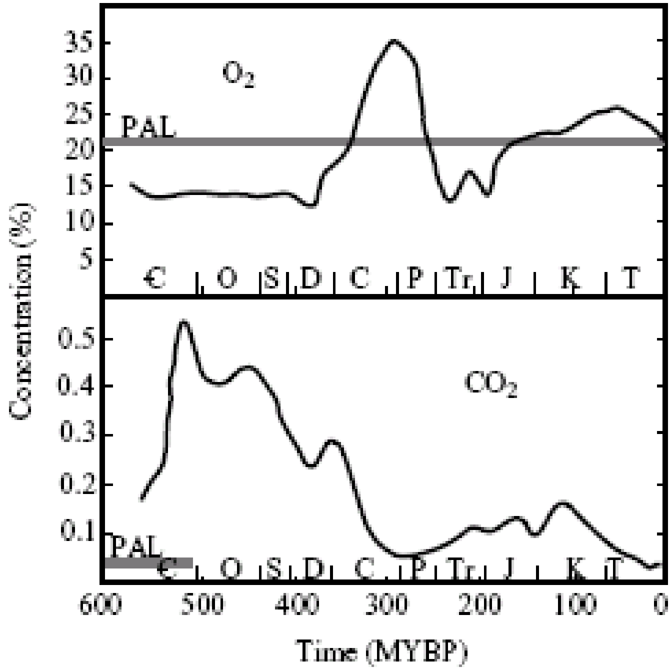
- **Rise of atmospheric O_2 linked to evolution of life:**
  - **400 My B.P. O_2 high enough to form an ozone layer**
  - **400 to 300 My B.P.: first air breathing lung fish & primitive amphibians**

- **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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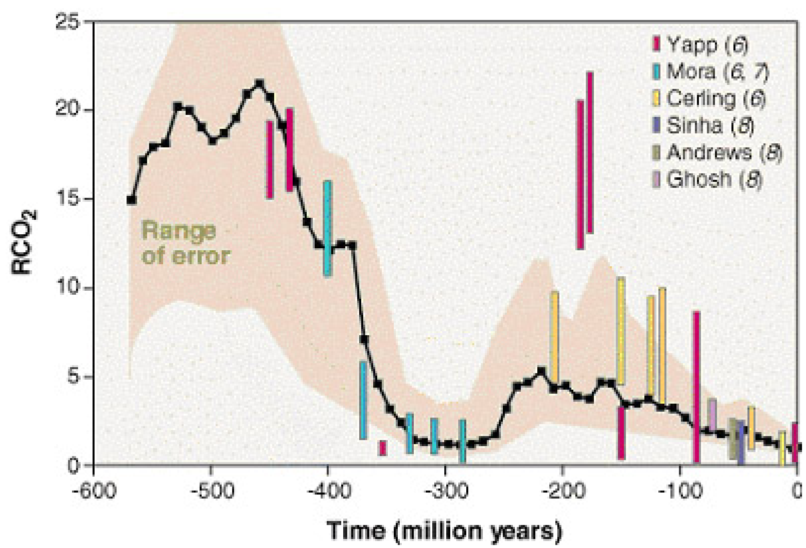
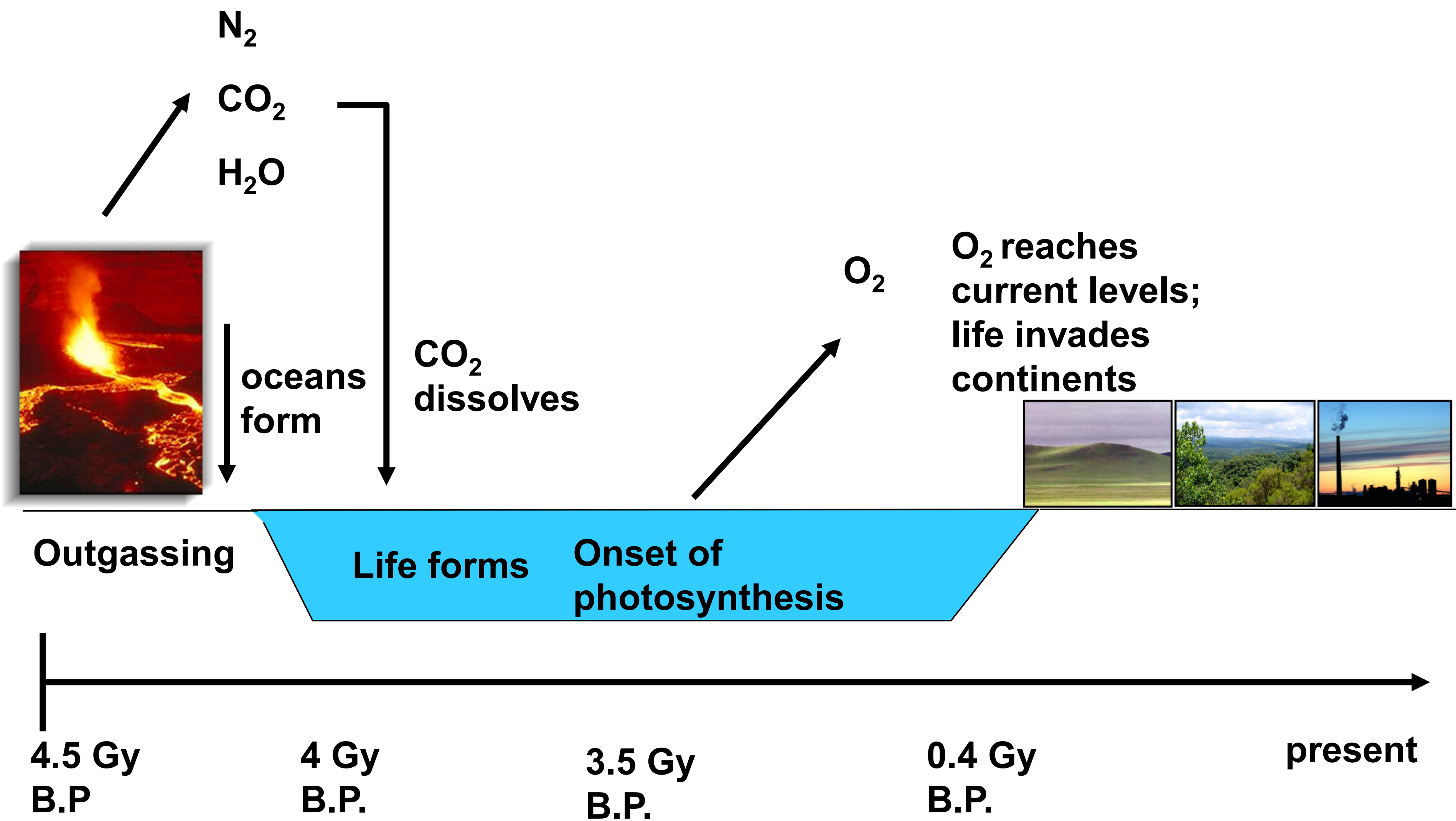


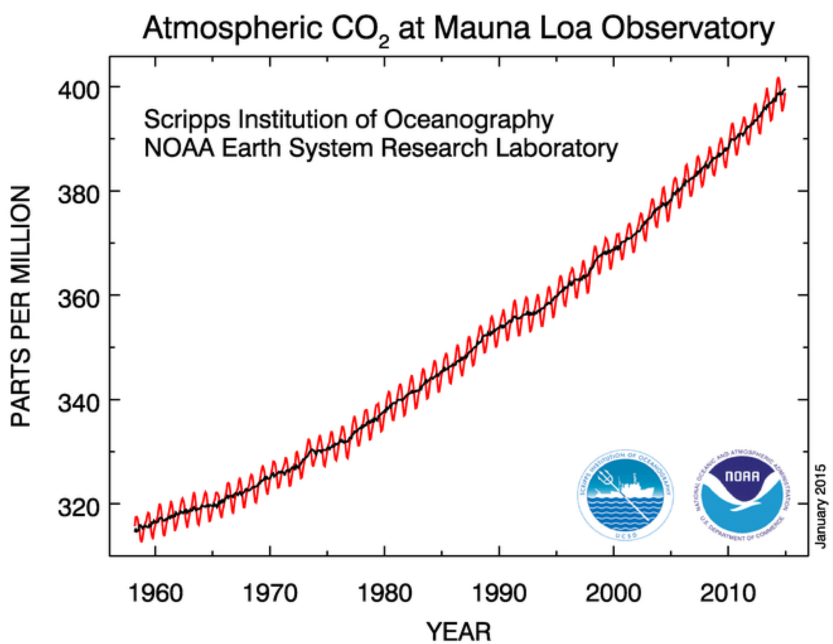
From R. Berner, *Science,* 276, 544, 1997.

Geological Evolution of Earth's Atmosphere:
Human Influence

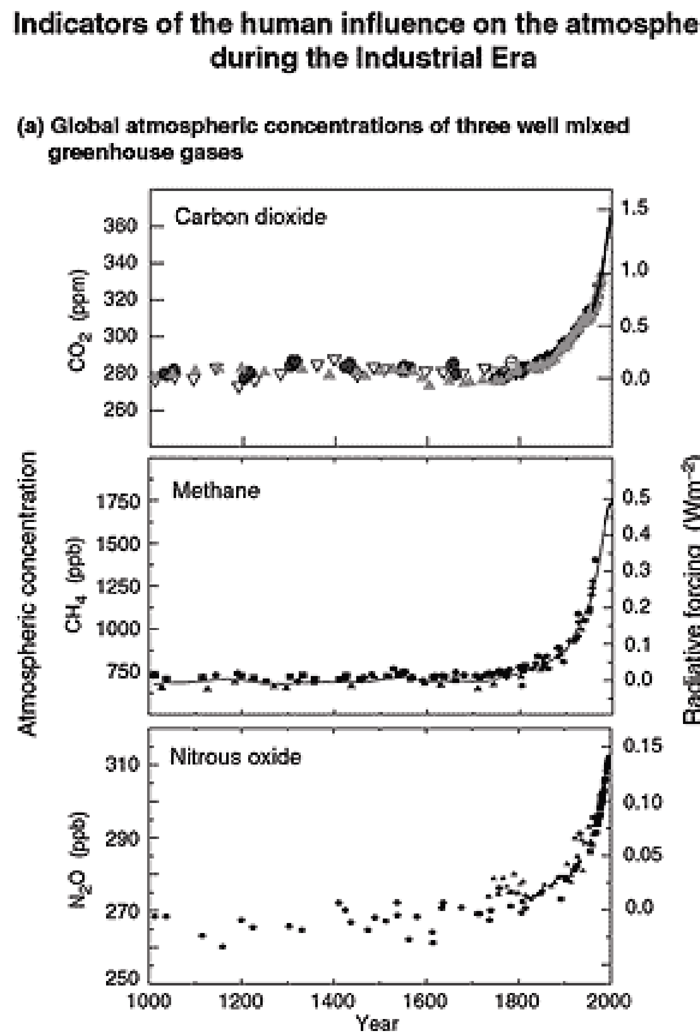


Earth’s Atmosphere – Effect of Humans

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



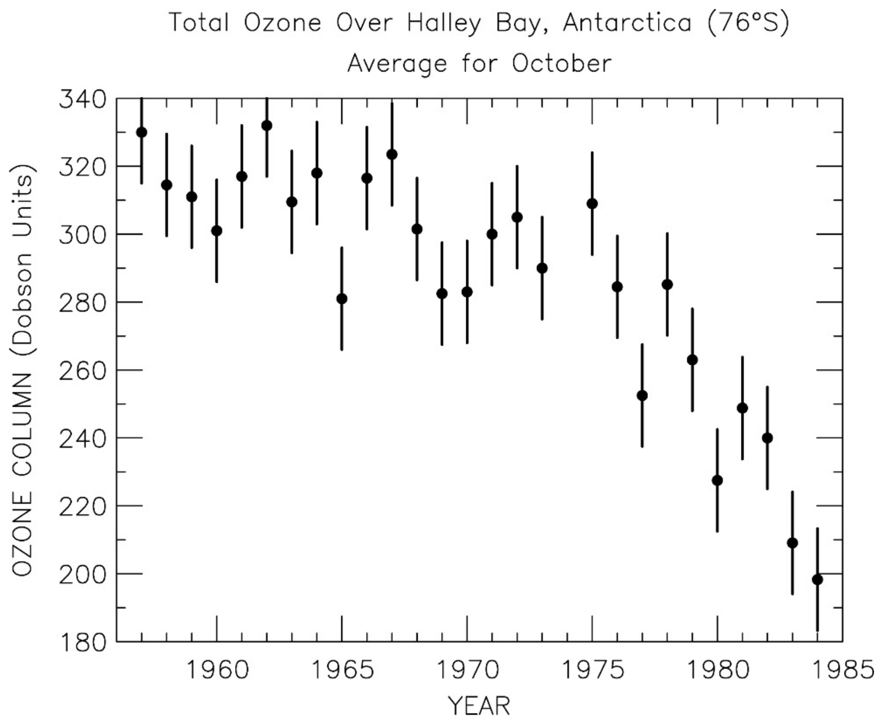
Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://www.esrl.noaa.gov/gmd/ccgg/trends



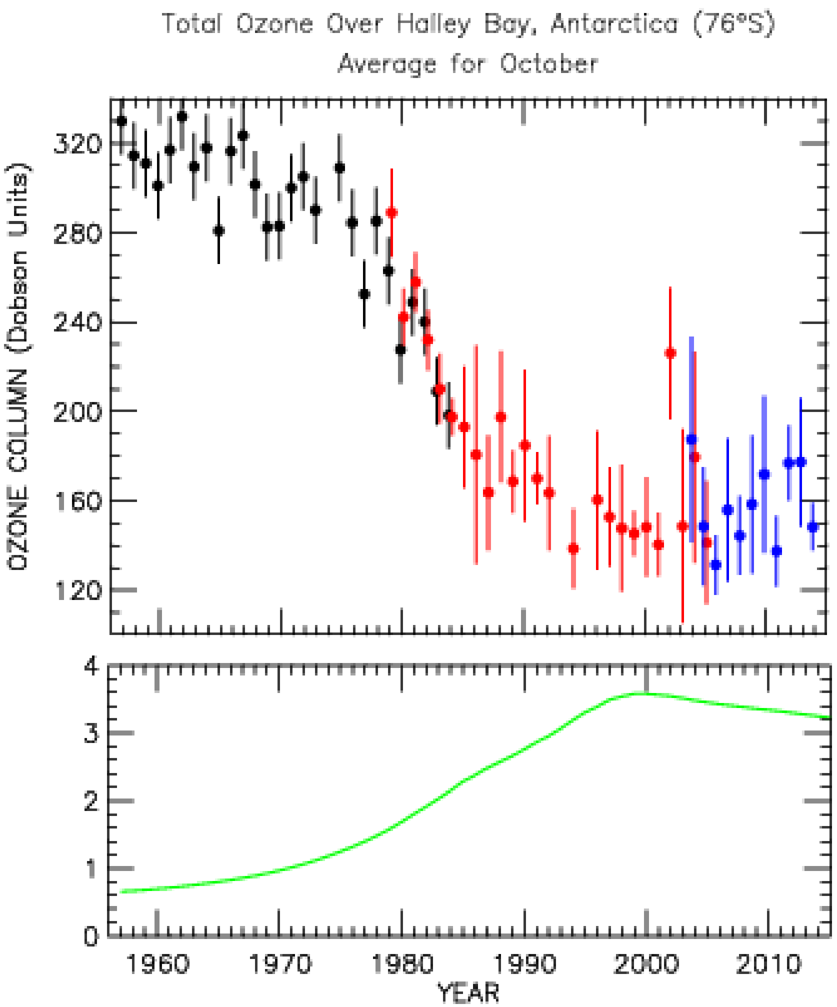
Climate Change 2001: IPCC Synthesis Report
http://www.grida.no/climate/ipcc_tar/vol4/english/index.htm

Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation



Update



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

Earth's Atmosphere – Effect of Humans

Tropospheric Ozone – oxidant, lung irritant, harmful to crops

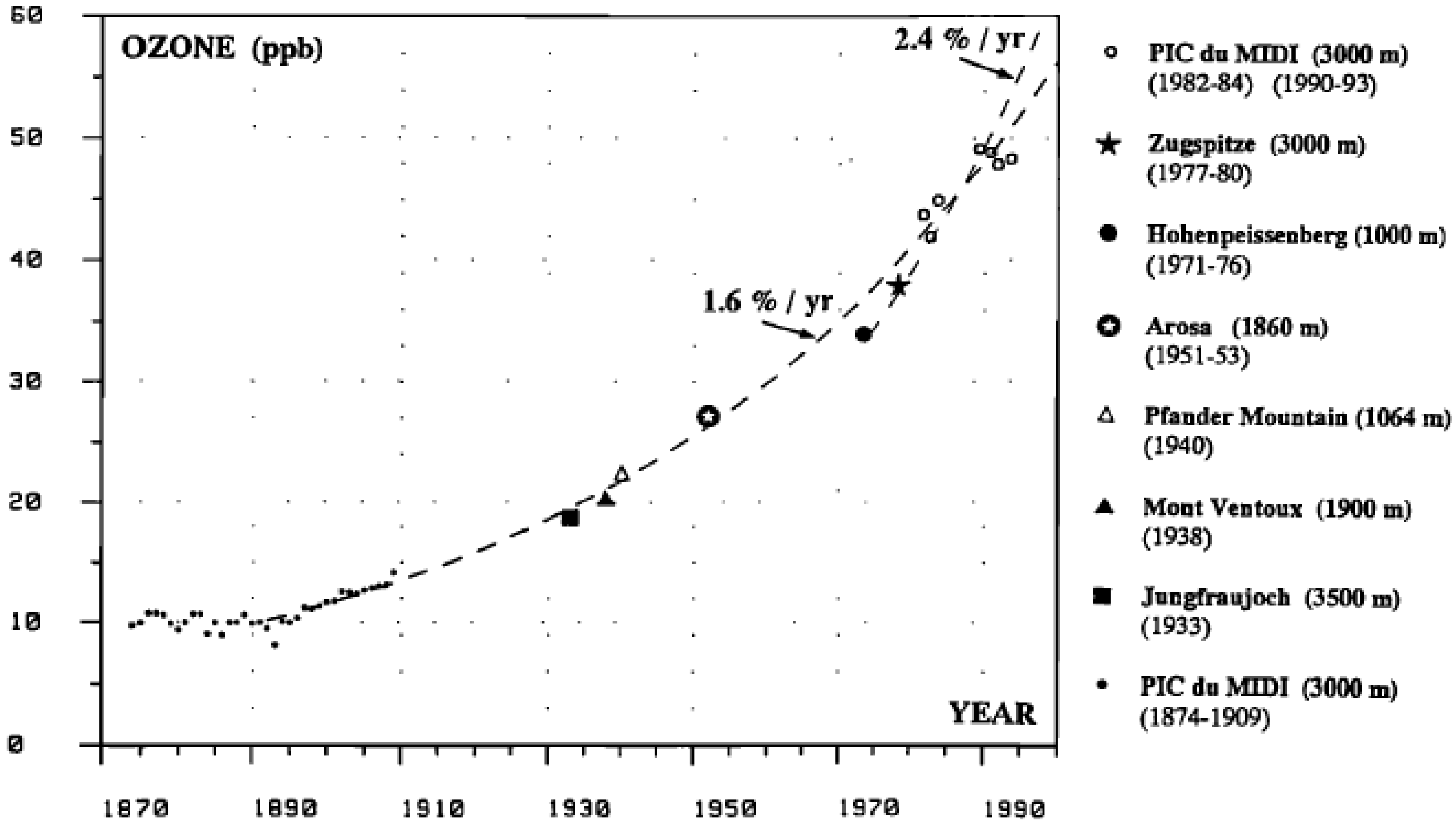


Figure 5. Ozone evolution in the free atmosphere over western Europe, from measurements at the Pic du Midi and in various European stations at high altitudes (see text).

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

Methane on Mars

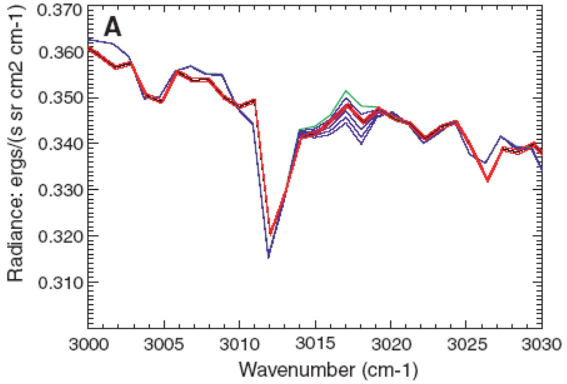
Report of ~50 ppb of CH_4 on Mars !

- Reported CH_4 not uniform:
  - average abundance of ~10 ppb

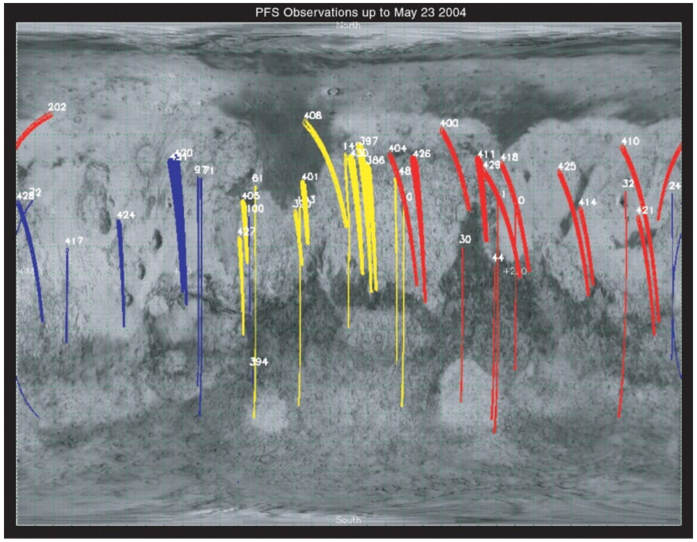
- **CH$_4$ lifetime on Mars ⇒ ~600 years**
  Loss due to oxidation by OH, O(^{1}D), & solar UV

  Short lifetime implies an *active source*

- Is this active source due to:
  - today's biology ?
  - present release from methane clathrates (past biology) ?
  - low temperature serpentinization (H_2+CO→CH_4) ?
    (would need high pressure & catalyst)



Synthetic spectra computed for 0 ppbv (green curve) and for 10, 20, 30, 40, and 50 ppbv (blue curves) of methane, compared with the average measured spectrum (red curve). The CH_4 feature is at 3018 cm^{-1}.



Geographical Distribution of CH_4 on Mars:

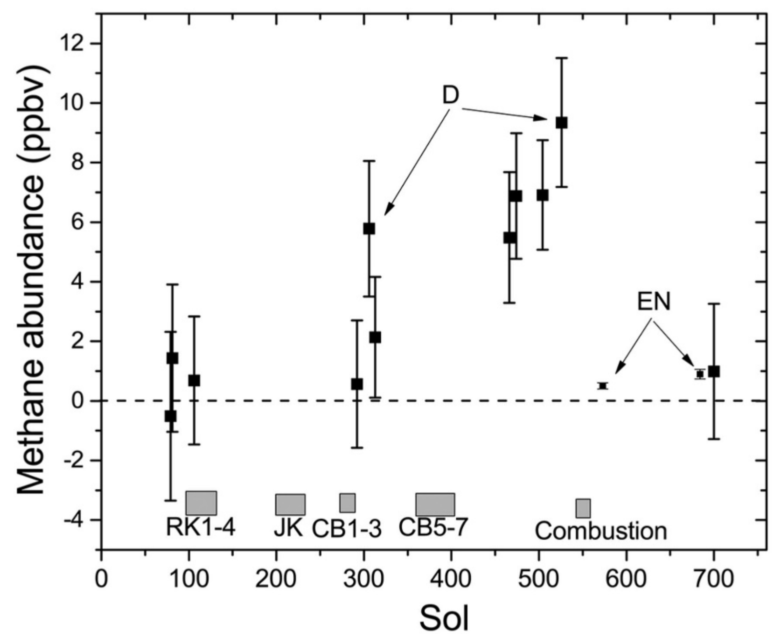
RED (high), YELLOW (medium), BLUE (low).

V. Formisano *et al*., Detection of Methane on Mars, *Science*, 2004

Methane on Mars

Webster *et al*., Mars Methane Detection and Variability at Gale Crater, *Science*, 16 Dec 2014

Reports of plumes or patches of methane in the Martian atmosphere that vary over monthly timescales have defied explanation to date. From in situ measurements made over a 20-month period by the Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars (SAM) instrument suite on Curiosity at Gale Crater, we report detection of background levels of atmospheric methane of mean value 0.69 ± 0.25 ppbv at the 95% confidence interval (CI). This abundance is lower than model estimates of ultraviolet (UV) degradation of accreted interplanetary dust particles (IDP's) or carbonaceous chondrite material. Additionally, in four sequential measurements spanning a 60-sol period, we observed elevated levels of methane of 7.2 ± 2.1 (95% CI) ppbv implying that Mars is episodically producing methane from an additional unknown source.



Next Lecture: Course Overview (Ross)

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, 18 (19 pages)

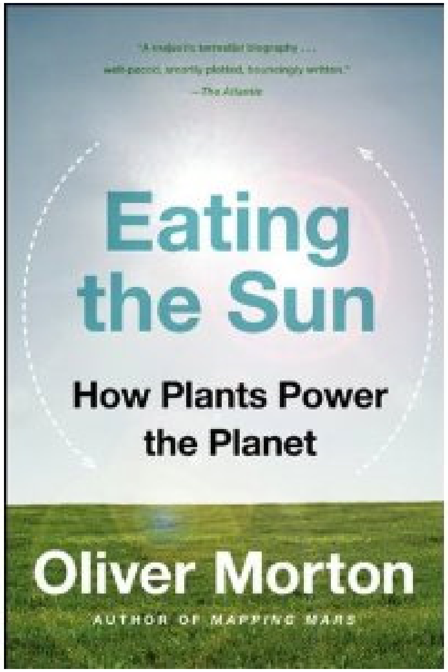
Note: ~40 pages of reading, per lecture, is about our norm

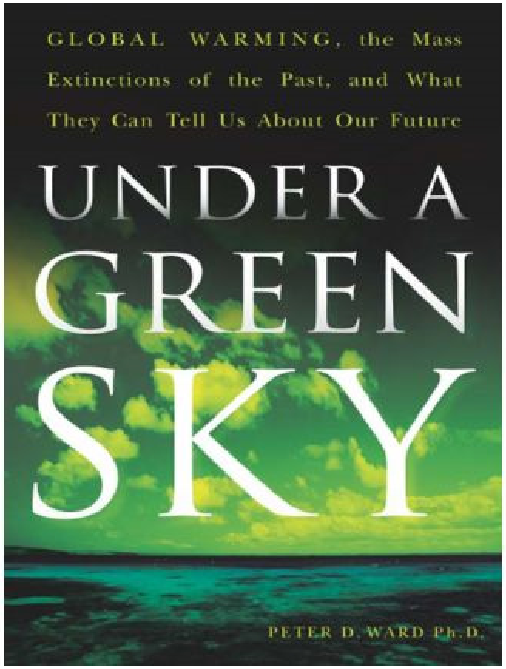
Admission Ticket for Lecture 2 is posted at:

http://www.atmos.umd.edu/~rjs/class/spr2015/admission_tickets/ACC_2015_admis_ticket_lecture_02.pdf

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