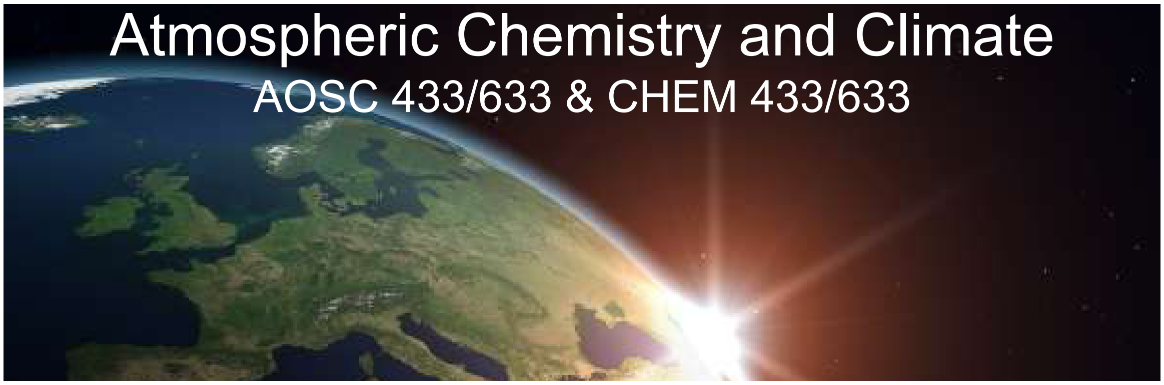
Atmospheric Chemistry and Climate

AOSC 433/633 & CHEM 433/633



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Web Site: http://www.atmos.umd.edu/~rjs/class/spr2013

Required Textbook: *Chemistry in Context: Applying Chemistry to Society*, American Chemical Society ⇒ **6th edition !**

Supplemental Texts:

Atmospheric Pollution by Mark Z. Jacobson

Global Warming: The Complete Briefing 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

Class Website

Date	Lecture Topic	Lecturer	Required Readings	Admis. Tickets	Lecture Notes	Learning Outcome	Problem Sets*	Additional Readings
01/24	Geological Evolution of Earth's Atmosphere	RJS	NPR article (our teaching philosophy!)		Lecture 1 ✓ Video	Lecture 1 QuizEgg		Sci American CH4 Mars & Titan May 2007; Hopes linger for Mars methane
01/29	Overview of Global Warming, Air Quality, & Ozone Depletion	RJS	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			Chemistry in Context, Ch 2 (pg 57 to 72); Sci American Why is there an ozone hole? Aug 2007; Kerr, Science, 2007; Bell *et al.*, EHP, 2008; Naming Convention for CFCs & Halons
01/31	Fundamentals of Earth's Atmosphere	TC	Chemistry in Context, Sections 1.1, 1.2, and 1.5; Jacobson, pg 50-64	AT 3 ✓	Lecture 3 × Video			Houghton, Ch 2

http://www.atmos.umd.edu/~rjs/class/spr2013

Lecture 1

24 January 2013

Organization Details

- Admission Tickets:
  - short set of questions, related to lecture; *turned in at start of each class*
  - posted on web page; straightforward if reading has been done
  - typically graded on a ~ 5, 10 or 15 point basis; *lowest three scores will be dropped*
  - can send us completed admission ticket prior to class via either email
- Problem Sets:
  - 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: we can not accept after solutions have been handed out (typically within ~7 days of the due date)
- Grading:
  - admission tickets: 10%
  - problem sets: 30%
  - in-class exam I and II: 20% each (closed book)
  - final exam: 20% (closed book)
  - collaboration policy posted on class website: problems sets & admission tickets should reflect your own work & understanding of the material
- Office hours:
  - Ross (CSS 2403) & Tim (CSS 2411) : Monday, 2:30 to 3:30 pm
  - Allison (Jull 2108): Wednesday, 4:00 to 5:00 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: we're generally quite busy just before class. We are usually available after class but Tues is better because weekly AOSC seminar is 3:30 pm on Thurs

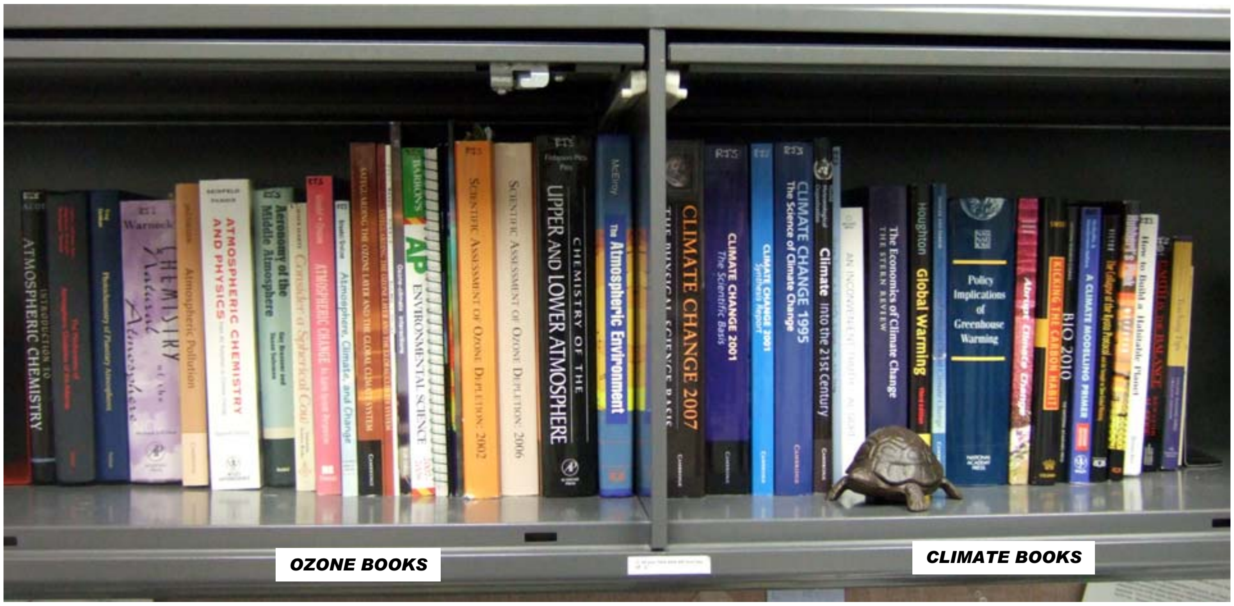
Organization Details, Continued

- Graduate Students:
  - ~8 page, single-spaced (not including references and figures) research paper
  - topic of student's choosing related to class material (instructors will be happy to consult and/or suggest topics)
  - due 9 May 2013 (last day of class)
  - presentation (either evening session or AOSC student seminar series)
  - paper & presentation will contribute to final grade in an amount equal to the weight of each exam
  - extra question on some problem sets
- Readings
  - All readings, except those from required text, will be posted on class webpage
  - We will also provided handouts of selected readings
  - 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

    Will not form the basis of any exam question
- Email
  - ***Please use ACC at start of subject line & send emails to all 3 of us***

Implemented last year: recording of lectures, evening sessions, & Google Groups
***New for this year*: Learning Outcome Quiz for each lecture**

Why Five Books And So Many Readings?

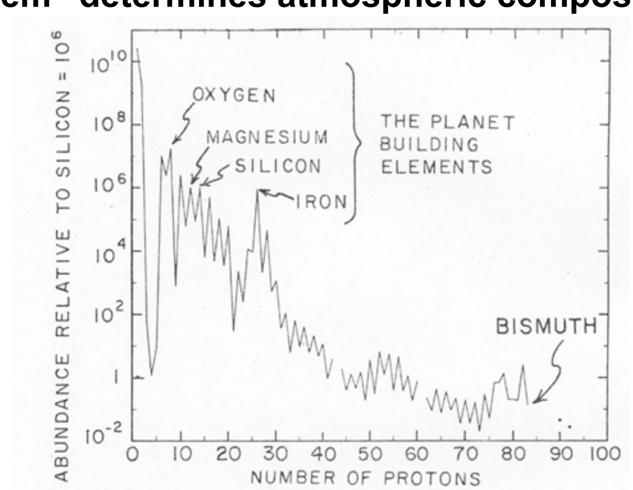


Geological Evolution of Earth's Atmosphere:
"In the Beginning"

- **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**

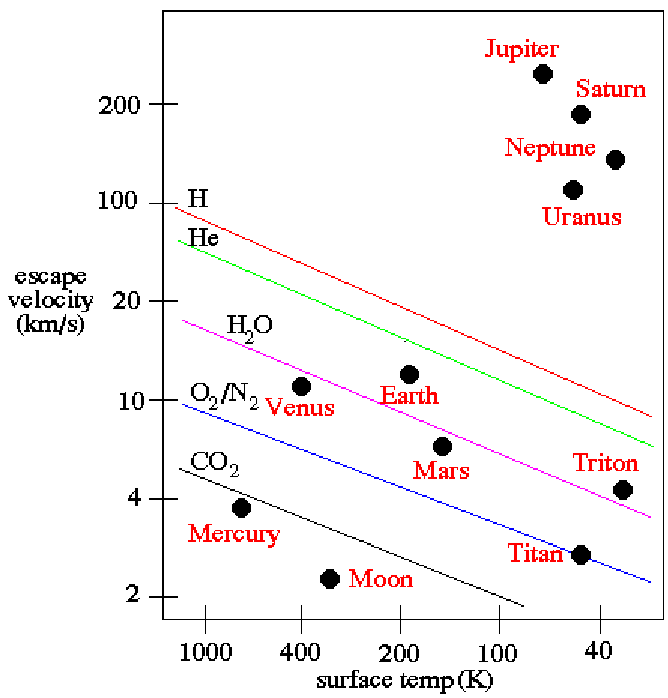


From "How to Build a Habitable Planet"
By W.S. Broecker, ELDIGIO Press, pg 57

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

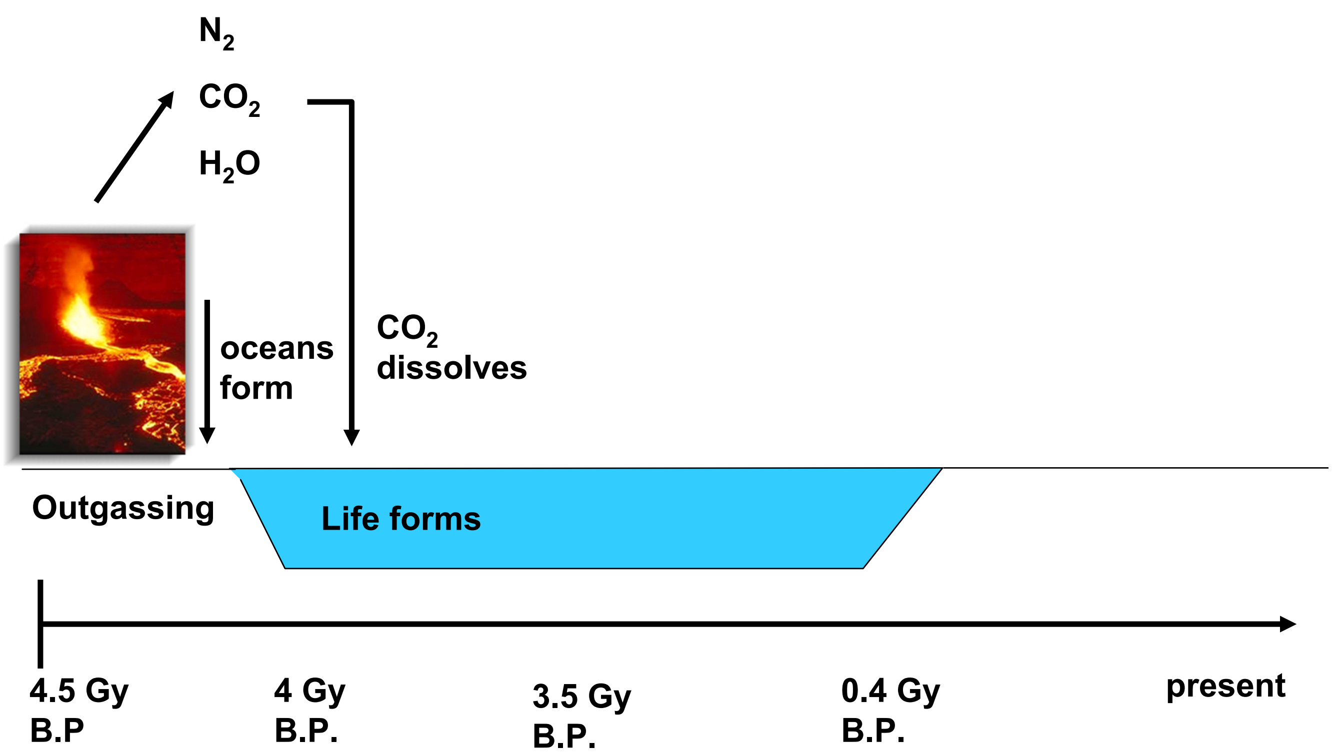
	Earth	Venus	Mars
Radius (km)	6400	6100	3400
Surface Pressure (atm)	1	91	0.007
Surface Temperature (K)	~15 °C	~ 460 °C	−140 °C to 20 °C
N_2 (mol/mol)	0.78	3.4×10^{-2}	2.7×10^{-2}
O_2 (mol/mol)	0.21	6.9×10^{-5}	1.3×10^{-3}
CO_2 (mol/mol)	3.7×10^{-4}	0.96	0.95
H_2O (mol/mol)	1×10^{-2}	3×10^{-3}	3×10^{-4}
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:
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 – $\sum$

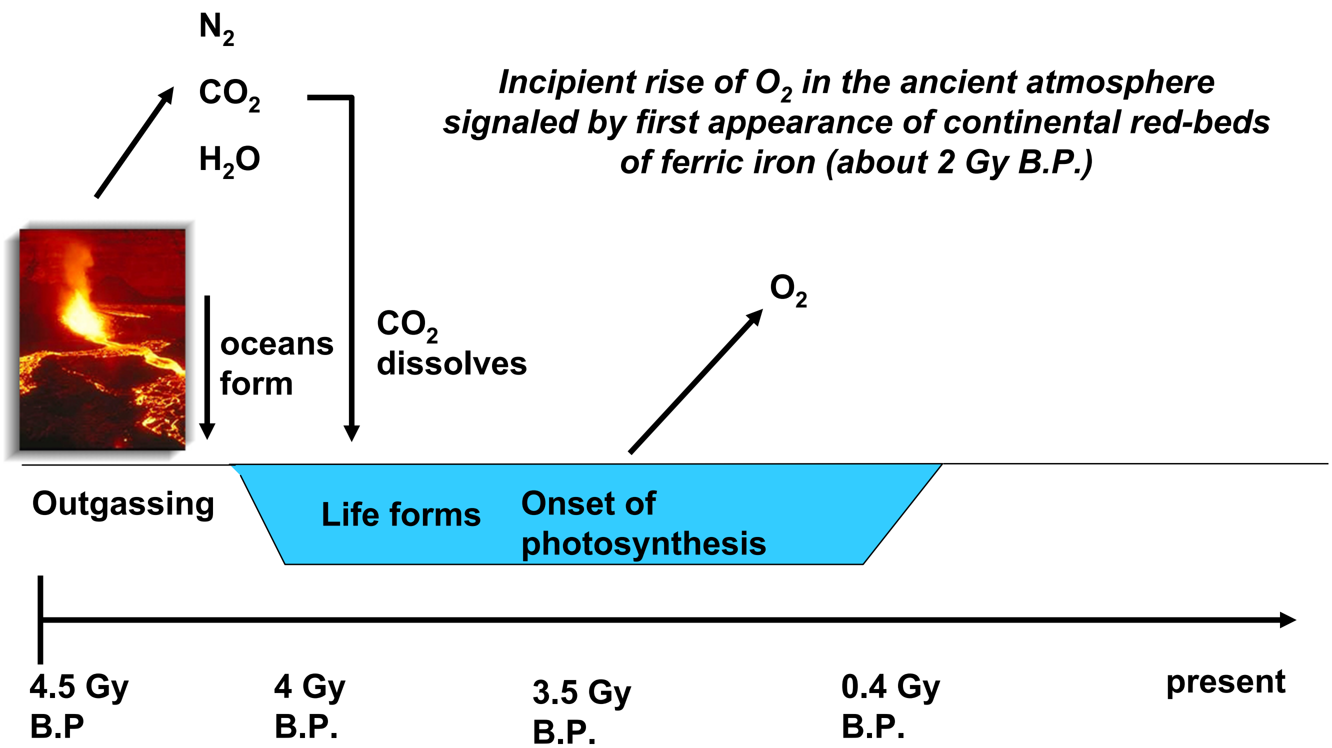
Note: there are some exceptions to this rule, such as oxygen in peroxides

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 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

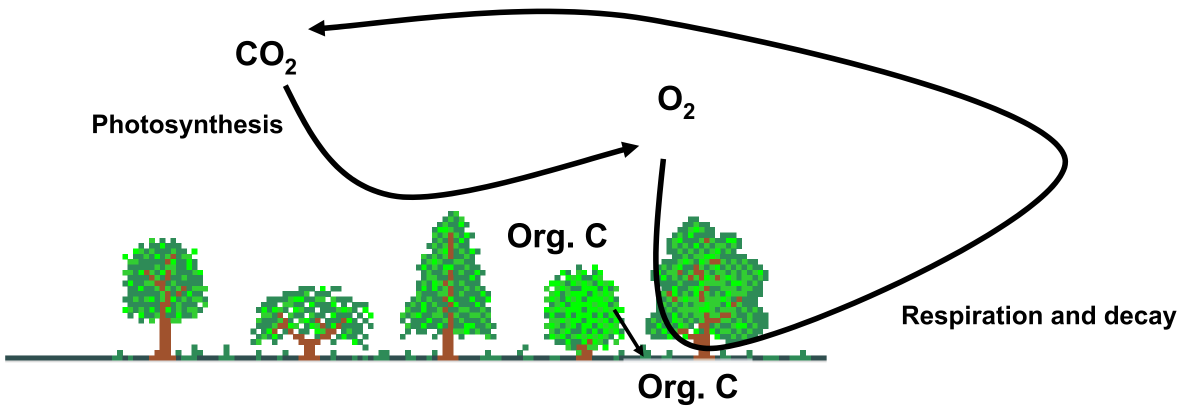
- **Photosynthesis: Source of O_2**

  $nCO_2 + nH_2O + \text{energy} \rightarrow (CH_2O)n + n\,O_2$

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

  $(CH_2O)n + n\,O_2 \rightarrow nCO_2 + nH_2O + \text{energy}$

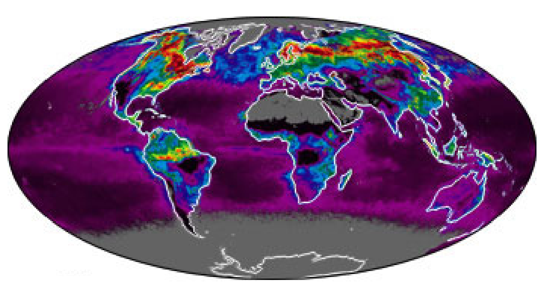
Typically, n = 6, so $C_6H_{12}O_6$ represents "organic matter" from a geological perspective



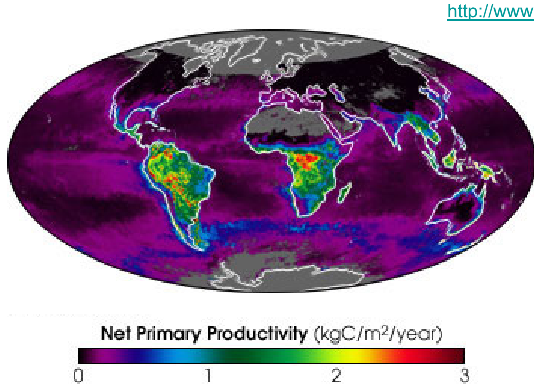
Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

- **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}



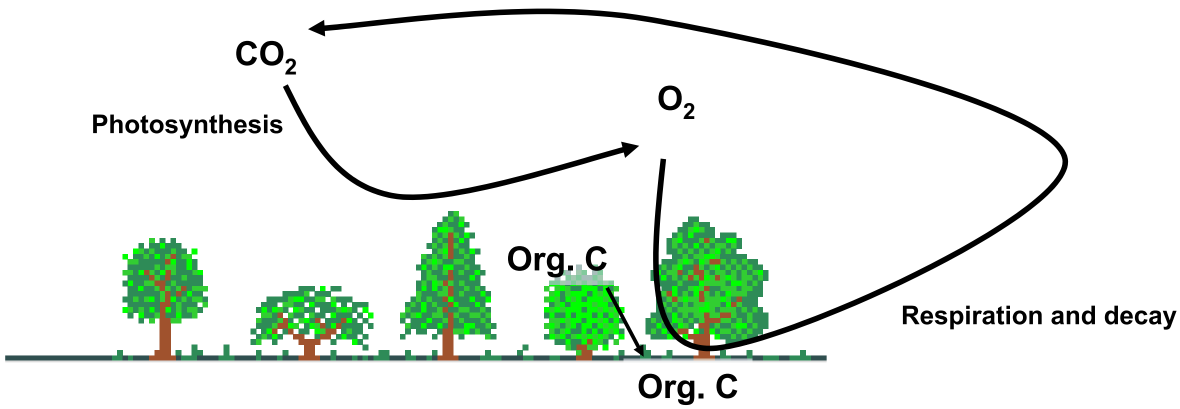
http://www.globalcarbonproject.org/science/figures/FIGURE9.htm



Global net primary productivity (NPP) based on space-based measurements obtained by the NASA MODIS satellite instrument.

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})**
  $\approx$ 8,000 yr



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 $\rightarrow$

$C_6H_{12}O_6$ (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*

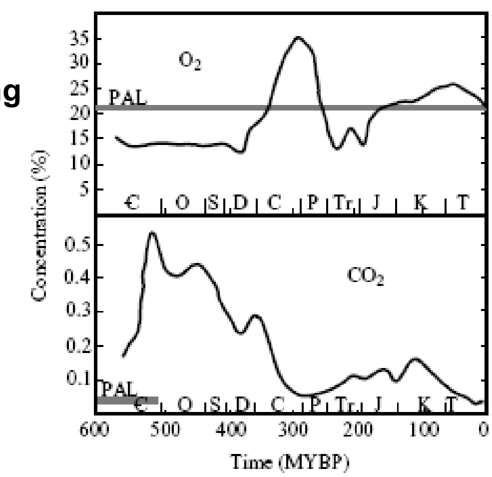
- **Rise of atmospheric O_2 linked to evolution of life:**
  - 400 My B.P. O_2 high enough to form an ozone layer
  - 400 to 300 My B.P.: first air breathing lung fish & primitive amphibians

- **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 O_2 on Geological Time Scales*

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

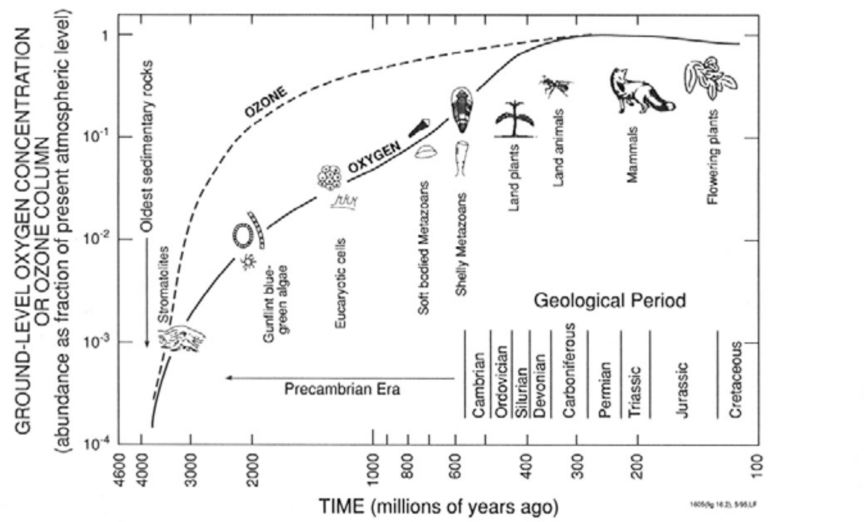


Figure 16.3. *Probable evolution of the oxygen and ozone abundance in the atmosphere (fraction of present levels) during the different geological periods of the Earth's history (Wayne, 1991; reprinted by permission of Oxford University Press).*

Geological Evolution of Earth's Atmosphere: *Atmospheric 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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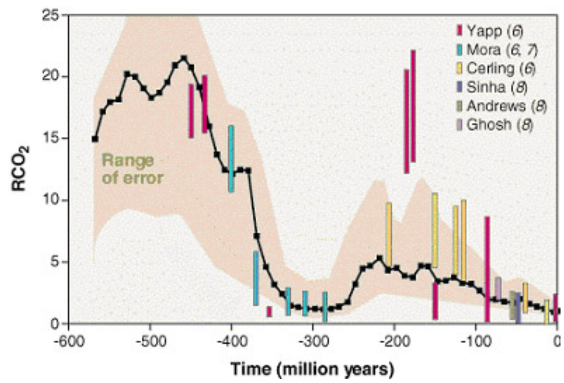
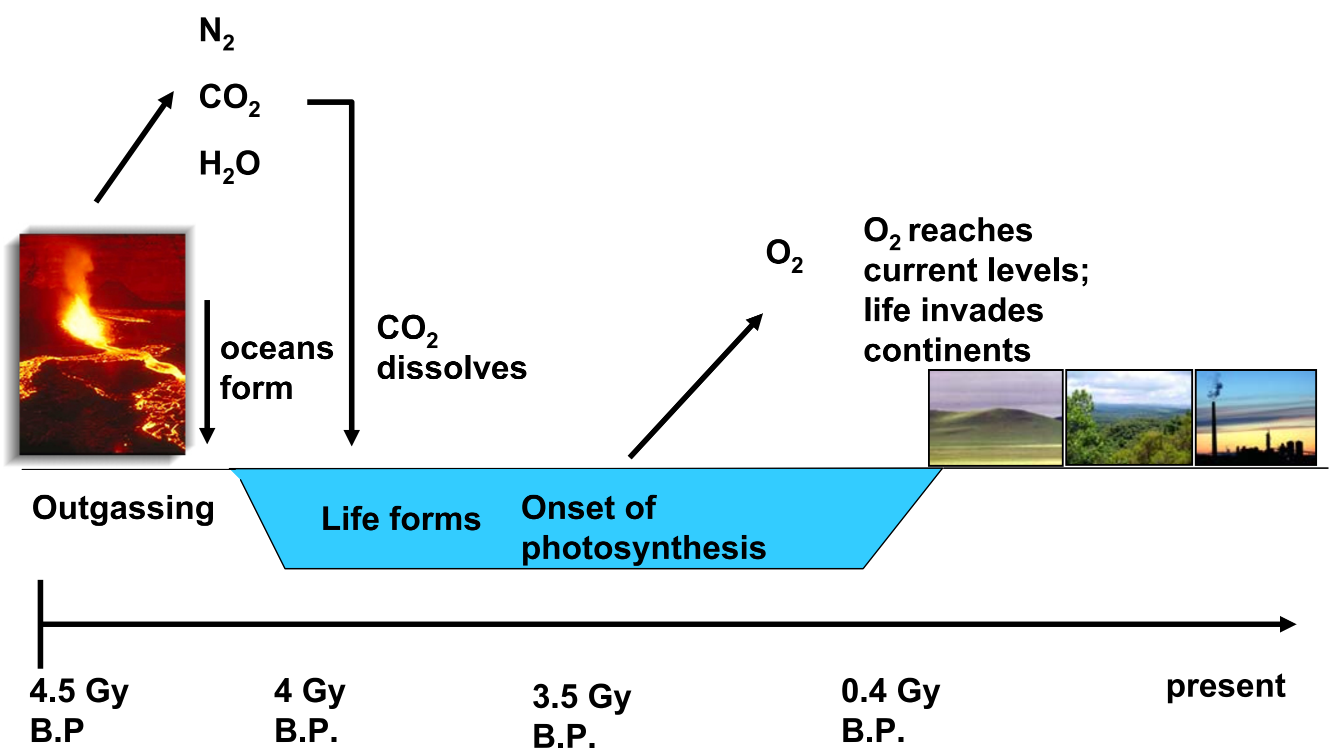


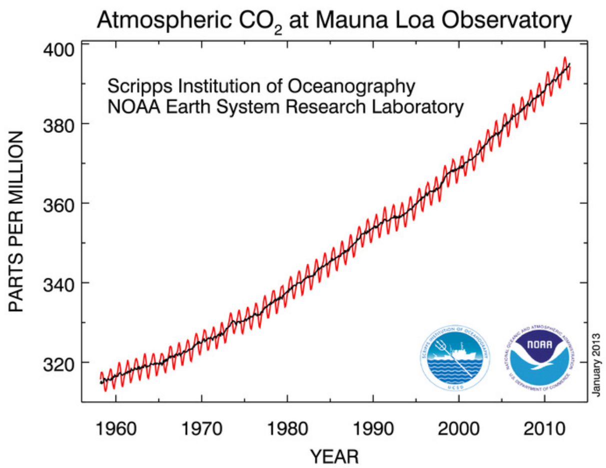
From R. Berner, *Science,* 276, 544, 1997.

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

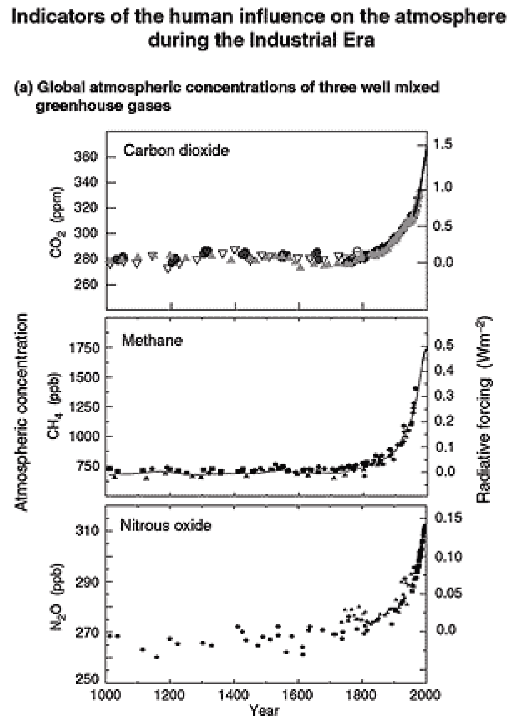


Earth's Atmosphere – Effect of Humans

CO_2: ~394 parts per million (ppm) and rising !



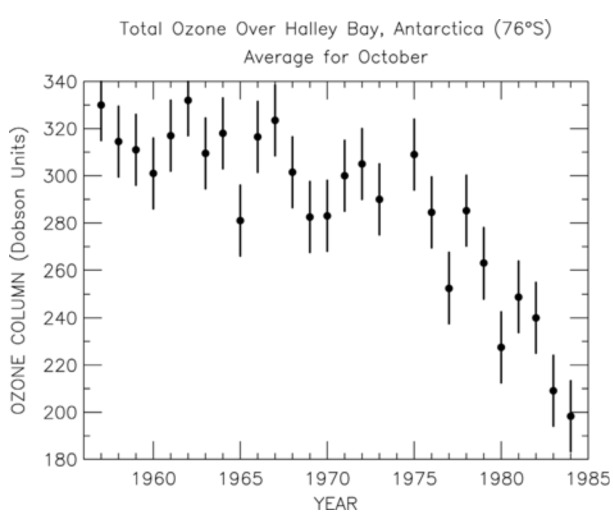
Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://www.esrl.noaa.gov/gmd/ccgg/trends



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

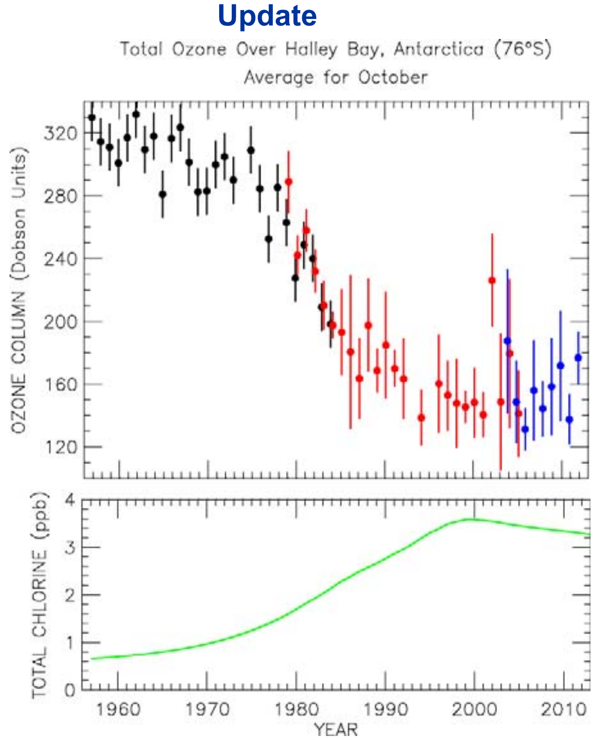
Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation



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

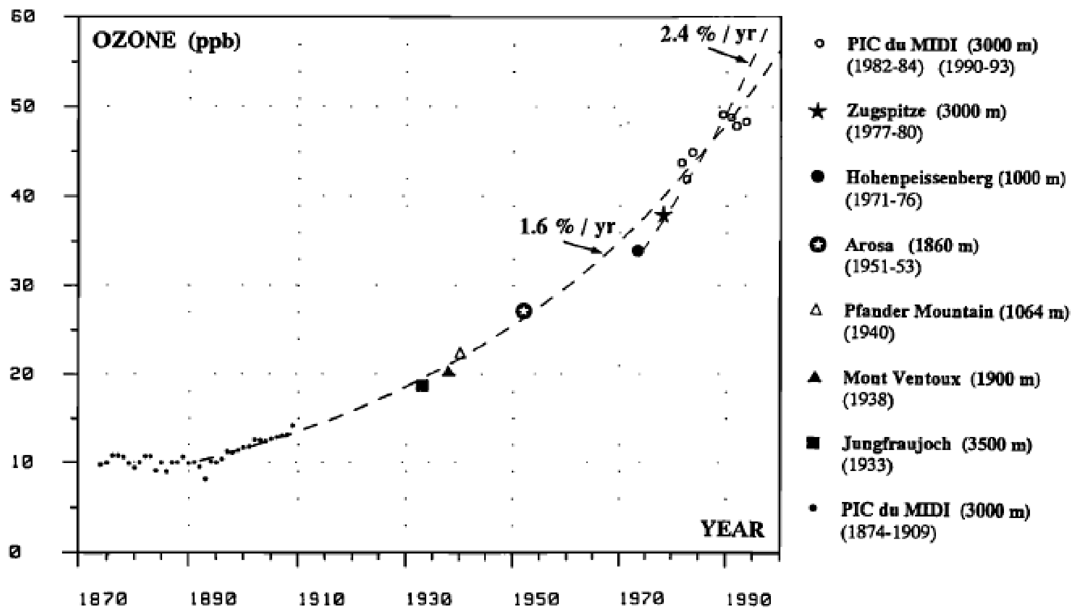


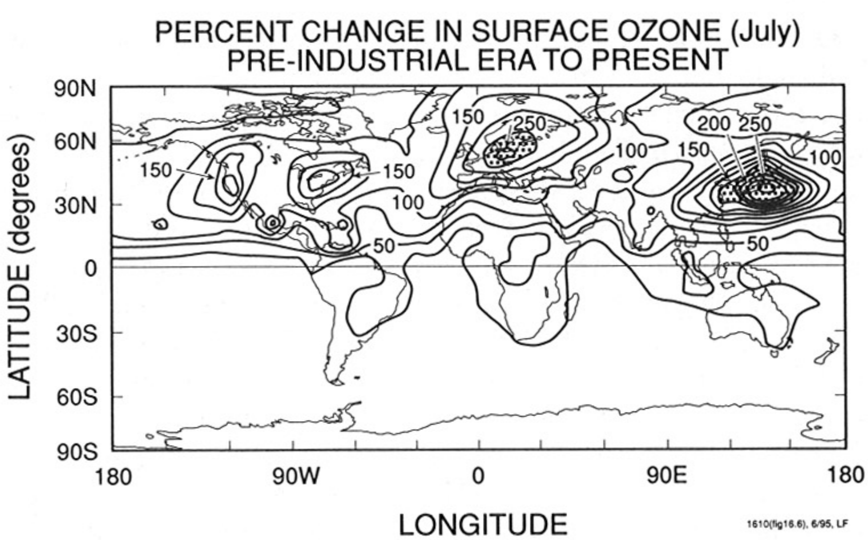
Figure 5. Ozone evolution in the free atmosphere over western Europe, from measurements at the Pic du Midi and in various European stations at high altitudes (see text).

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

Earth's Atmosphere – Effect of Humans

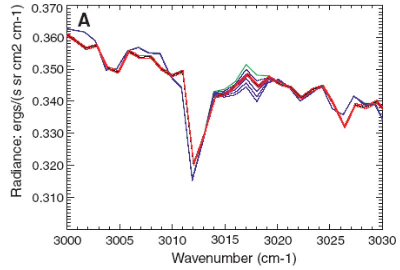
Tropospheric Ozone – oxidant, lung irritant, harmful to crops

Figure 16.8. Change (in percent) of the surface ozone concentration from the preindustrial era to present day for the month of July calculated by the IMAGES 3D chemical-transport model (based on data from Müller and Brasseur, 1995).



Atmospheric Chemistry and Global Change, NCAR, 1999

Methane on Mars



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}.

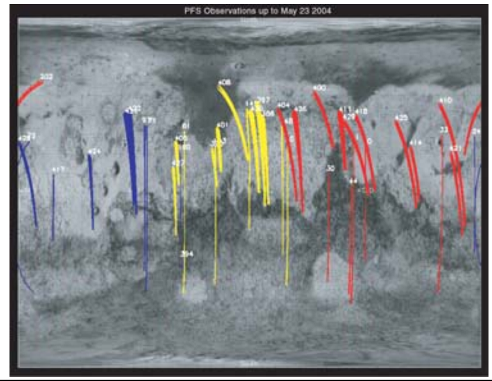
Report of ~50 ppb of CH_4 on Mars !

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

- **CH_4 lifetime on Mars ⇒ ~600 years**
  Loss due to oxidation by OH, $O(^1D)$, & 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)



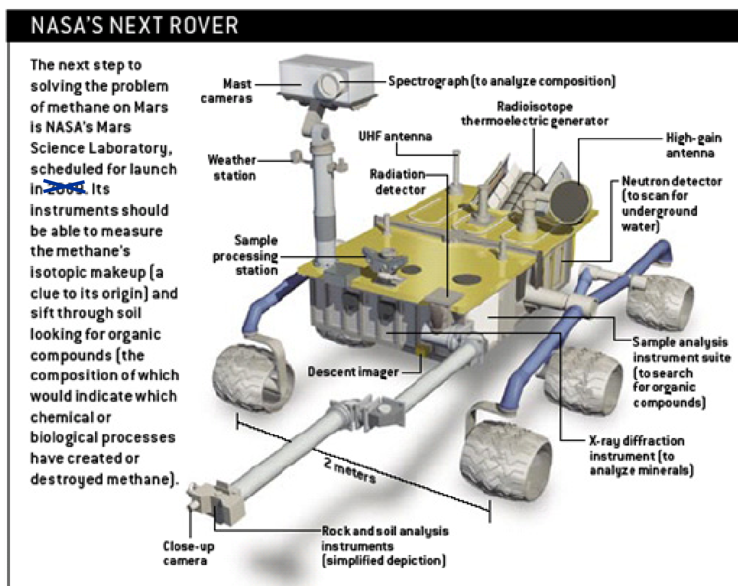
Geographical Distribution of CH_4 on Mars:
RED (high), YELLOW (medium), BLUE (low).

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

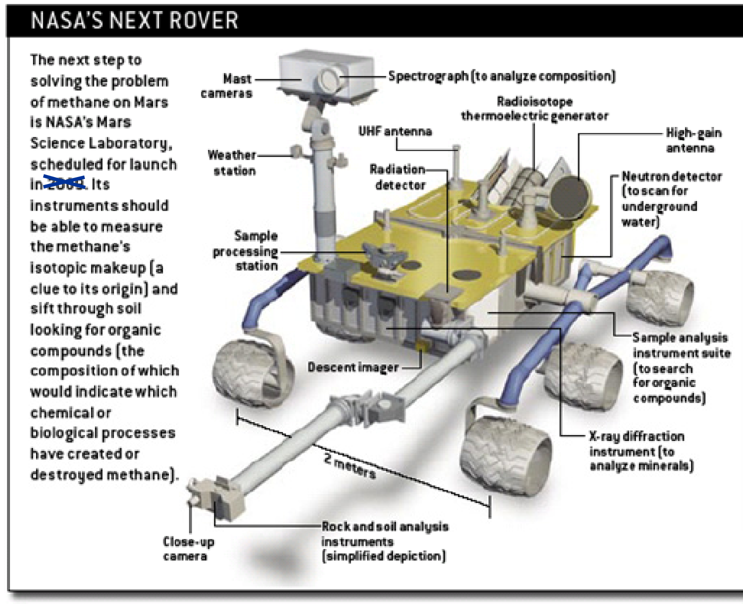
Landed 26 November 2011

http://www.nasa.gov/mission_pages/msl

The Mars Science Laboratory will assess whether Mars ever was or is today an environment able to support microbial life



From "The Mystery of Methane on Mars & Titan", S. K. Atreya, today's "additional reading" material.



Landed 6 August 2012

http://www.nasa.gov/mission_pages/msl

The Mars Science Laboratory will assess whether Mars ever was or is today an environment able to support microbial life

From "The Mystery of Methane on Mars & Titan", S. K. Atreya, today's "additional reading" material.

The team said that with 95% certainty, Martian methane does not exceed 5 parts per billion (ppb), a level that could more readily be explained by non-biological geochemical reactions or by comet impacts delivering pulses of the gas from space. And the true value could be zero. "Bottom line is we have no detection of methane so far," says Chris Webster of the Jet Propulsion Laboratory in Pasadena, California

5 Nov 2012, Nature http://www.nature.com/news/hopes-linger-for-mars-methane-1.11746

Next Lecture: Course Overview (Ross)

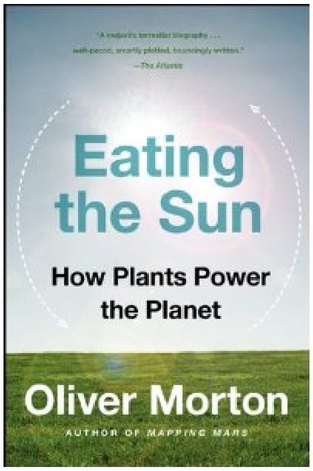
Readings: IPCC 2007 FAQ 1.1, 1.2, 1.3, 2.1, & 3.1 (11 pages)
EPA Air Quality Guide (11 pages)
WMO Ozone FAQ 1, 2, 3, 10, 15, 18 (16 pages)
Note: ~40 pages of reading, per lecture, is about our norm

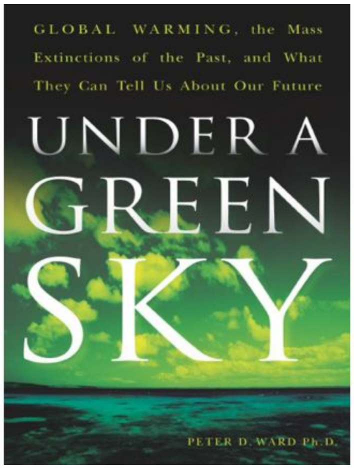
Admission Ticket for Lecture 2 is posted at:

http://www.atmos.umd.edu/~rjs/class/spr2013/admission_tickets/ACC_2013_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 source material for much of this lecture