### Class Website

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<th>Lecture Topic</th>
<th>Lecturer</th>
<th>Required Readings</th>
<th>Admis. Tickets</th>
<th>Lecture Notes</th>
<th>Learning Outcome</th>
<th>Problem Sets*</th>
<th>Additional Readings</th>
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<tr>
<td>01/04</td>
<td>Geologic Evolution of Earth's Atmosphere</td>
<td>RJS</td>
<td>NEP article (our teaching philosophy)</td>
<td></td>
<td>Lecture 1 Video</td>
<td>Lecture 1 Questions</td>
<td></td>
<td>Biogeochemistry Ch. 3 (pp 27-44)</td>
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<td>Biogeochemistry Ch. 3 (pp 27-44)</td>
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<tr>
<td>01/29</td>
<td>Overview of Global Warming, Air Quality, &amp; Ozone Depletion</td>
<td>RJS</td>
<td>IPCC 2007, FAQ (questions 1.1, 1.2, 2.1, 2.2, 2.3)</td>
<td></td>
<td>Lecture 2 Video</td>
<td></td>
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<td>Biogeochemistry Ch. 3 (pp 27-44)</td>
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<td>Biogeochemistry Ch. 3 (pp 27-44)</td>
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<tr>
<td>01/31</td>
<td>Fundamentals of Earth's Atmosphere</td>
<td>TC</td>
<td>Chemistry in Context, Sections 1.1, 1.2, and 1.2 (section pp 40-46)</td>
<td>AT 3 ✔</td>
<td>Lecture 3 Video</td>
<td></td>
<td></td>
<td>Biogeochemistry Ch. 3 (pp 27-44)</td>
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<td>Biogeochemistry Ch. 3 (pp 27-44)</td>
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</tbody>
</table>

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

**Lecture 1**

24 January 2013
• Admission Tickets:
  – short set of questions, related to lecture; \textit{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; \textit{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
  \textbf{Will not form the basis of any exam question}

• Email
  – \textit{Please use ACC at start of subject line & send emails to all 3 of us}

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

<table>
<thead>
<tr>
<th></th>
<th>Earth</th>
<th>Venus</th>
<th>Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (km)</td>
<td>6400</td>
<td>6100</td>
<td>3400</td>
</tr>
<tr>
<td>Surface Pressure (atm)</td>
<td>1</td>
<td>91</td>
<td>0.007</td>
</tr>
<tr>
<td>Surface Temperature (K)</td>
<td>~15 °C</td>
<td>~460 °C</td>
<td>−140 °C to 20 °C</td>
</tr>
<tr>
<td>N₂ (mol/mol)</td>
<td>0.78</td>
<td>3.4×10⁻²</td>
<td>2.7×10⁻²</td>
</tr>
<tr>
<td>O₂ (mol/mol)</td>
<td>0.21</td>
<td>6.9×10⁻⁵</td>
<td>1.3×10⁻³</td>
</tr>
<tr>
<td>CO₂ (mol/mol)</td>
<td>3.7×10⁻⁴</td>
<td>0.96</td>
<td>0.95</td>
</tr>
<tr>
<td>H₂O (mol/mol)</td>
<td>1×10⁻²</td>
<td>3×10⁻³</td>
<td>3×10⁻⁴</td>
</tr>
<tr>
<td>SO₂ (mol/mol)</td>
<td>1×10⁻⁹</td>
<td>1.5×10⁻⁴</td>
<td>Nil</td>
</tr>
<tr>
<td>Cloud Composition</td>
<td>H₂O</td>
<td>H₂SO₄</td>
<td>Mineral Dust</td>
</tr>
</tbody>
</table>

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Geological Evolution of Earth’s Atmosphere: 
*Outgassing*

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 Gy</td>
<td>Outgassing</td>
</tr>
<tr>
<td>4.0 Gy</td>
<td>Outgassing</td>
</tr>
<tr>
<td>3.5 Gy</td>
<td>Outgassing</td>
</tr>
<tr>
<td>0.4 Gy</td>
<td>Outgassing</td>
</tr>
<tr>
<td>Present</td>
<td>Outgassing</td>
</tr>
</tbody>
</table>

**Outgassing**

- **N₂**
- **CO₂**
- **H₂O**

**Life forms**

**Decreasing oxidation number (reduction reactions)**

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3</td>
<td>NH₃ (Ammonia)</td>
</tr>
<tr>
<td>0</td>
<td>N₂</td>
</tr>
<tr>
<td>+1</td>
<td>N₂O (Nitrous oxide)</td>
</tr>
<tr>
<td>+2</td>
<td>NO (Nitric oxide)</td>
</tr>
<tr>
<td>+3</td>
<td>HONO (Nitrous acid NO₂⁻)</td>
</tr>
<tr>
<td>+4</td>
<td>NO₂ (Nitrogen dioxide)</td>
</tr>
<tr>
<td>+5</td>
<td>HNO₃ (Nitric acid NO₃⁻)</td>
</tr>
</tbody>
</table>

**Increasing oxidation number (oxidation reactions)**

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

**Oxidation state of a compound:** \( \Sigma = -2 \times \# \text{O atoms} + 1 \times \# \text{H atoms} \)

Oxidation of element = Electrical Charge – \( \Sigma \)

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)**

<table>
<thead>
<tr>
<th>-4</th>
<th>0</th>
<th>+2</th>
<th>+4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>CH₂O</td>
<td>CO</td>
<td>CO₂</td>
</tr>
<tr>
<td>Methane</td>
<td>Formaldehyde</td>
<td>Carbon Monoxide</td>
<td>Carbon dioxide</td>
</tr>
</tbody>
</table>

**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

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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*

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.)

- $N_2$
- $CO_2$
- $H_2O$
- $O_2$

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.

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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 O₂**
  
  \[ \text{nCO}_2 + \text{nH}_2\text{O} + \text{energy} \rightarrow (\text{CH}_2\text{O})\text{n} + \text{n O}_2 \]

- **Respiration and Decay: Sink of O₂**
  
  \[ (\text{CH}_2\text{O})\text{n} + \text{n O}_2 \rightarrow \text{nCO}_2 + \text{nH}_2\text{O} + \text{energy} \]

  Typically, \( n = 6 \), so \( \text{C}_6\text{H}_{12}\text{O}_6 \) represents “organic matter” from a geological perspective.

*Net primary productivity of organic matter:*

\[ 6 \text{ CO}_2 + 6 \text{ H}_2\text{O} + \text{hv} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2 \text{ is } \sim 57 \times 10^{15} \text{ g C yr}^{-1} \]

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:
  \[ 6 \text{ CO}_2 + 6 \text{ H}_2\text{O} + \text{hv} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2 \text{ is } \approx 57 \times 10^{15} \text{ g C yr}^{-1} \]
  Production of atmospheric \( \text{O}_2 \) is therefore \( \approx 152 \times 10^{15} \text{ g O}_2 \text{ yr}^{-1} \)

- Mass \( \text{O}_2 \) in atmosphere = \( 0.21 \times (5.2 \times 10^{21} \text{ g}) \times (32 / 29) \approx 1.2 \times 10^{21} \text{ g} \)

- Lifetime of atmospheric \( \text{O}_2 \) due to biology = \( 1.2 \times 10^{21} \text{ g} / (152 \times 10^{15} \text{ g O}_2 \text{ yr}^{-1}) \approx 8,000 \text{ yr} \)

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

1 Pg = \( 10^{15} \) G

**Atmosphere:**

- \( \text{CO}_2 : 2130 \text{ Pg O}, 800 \text{ Pg C} \)
- \( \text{O}_2 : 1.2 \times 10^{6} \text{ Pg O}_2 \)

**Organic Carbon : Biosphere**

- 700 Pg C, 933 Pg O

**Organic Carbon : Soil + Oceans**

- 3000 Pg C, 4000 Pg O

Atmospheric \( \text{O}_2 \) reservoir much larger than \( \text{O}_2 \) content of biosphere, soils, and ocean; therefore, some other process must control atmospheric \( \text{O}_2 \)
Geological Evolution of Earth’s Atmosphere:
Oxygen Reservoirs & Pathways

Atmosphere:
\[ \text{O}_2 : 1.2 \times 10^6 \text{ Pg O}_2 \]

1 Pg = 10^{15} G

Burial of organic matter is source of atmospheric O₂:
\[ 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{Energy} \rightarrow \text{C}_6\text{H}_12\text{O}_6 \text{ (buried)} + 6\text{O}_2 \text{ (atmosphere)} \]

O₂ Lifetime \approx 4 million years

Sediments: Buried Organic Carbon
\[ \text{O}_2 : \sim 32 \times 10^6 \text{ Pg O} \]

Weathering of mantle is sink of atmospheric O₂:
For example:
\[ \text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \]

Crust and Mantle: Oxides of Fe, Si, S, Mg, etc:
\[ \text{FeO, Fe}_2\text{O}_3, \text{FeSiO}_3, \text{SiO}_4, \text{MgO}, \text{etc} \]
This is where the bulk of the oxygen resides!

Geological Evolution of Earth’s Atmosphere:
Atmospheric O₂ on Geological Time Scales

• Rise of atmospheric O₂ linked to evolution of life:
  – 400 My B.P.: O₂ 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 O₂ 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:
\[ \text{CH}_4 \Rightarrow \text{CO}_2 \text{ with time scale of } \sim 9 \text{ years} \]

Geological Evolution of Earth’s Atmosphere:  
*Atmospheric O₂ on Geological Time Scales*

- Rise of atmospheric O₂ linked to evolution of life:

![Graph showing the evolution of oxygen and ozone abundance in the atmosphere over geological time.](image)

*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 CO₂ 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: δ¹³C 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 CO₂ on Geological Time Scales

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- Development of vascular land plants
- Plants became bigger and bigger and less reliant on water
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Geological Evolution of Earth’s Atmosphere:

Human Influence

N₂

CO₂

H₂O

oceans form

CO₂ dissolves

O₂ 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

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Earth’s Atmosphere – Effect of Humans

**CO₂:** ~394 parts per million (ppm) and rising!

![Atmospheric CO₂ at Mauna Loa Observatory](image1)

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

**Stratospheric Ozone – shields surface from solar UV radiation**

Update


![Total Ozone Over Halley Bay, Antarctica (76°S)](image2)

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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

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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

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Methane on Mars

Report of ~50 ppb of CH₄ on Mars!

- Reported CH₄ not uniform:
  - average abundance of ~10 ppb

- CH₄ 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 (H₂+CO→CH₄)?
  (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 CH₄ feature is at 3018 cm⁻¹.

Geographical Distribution of CH₄ on Mars:
RED (high), YELLOW (medium), BLUE (low).

From “The Mystery of Methane on Mars & Titan”, S. K. Atreya, today’s “additional reading” material.

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

Launched 26 Nov 2011
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
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

From “The Mystery of Methane on Mars & Titan”, S. K. Atreya, today’s “additional reading” material.
Source Material

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

[Image of book covers]

http://www.amazon.com/Eating-Sun-Plants-Power-Planet/dp/007163657/ref=sr_1_1?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?ie=UTF8&qid=1359326345&sr=1-1&keywords=under+a+green+sky

and provided source material for much of this lecture