

## Lecture 35

### Differentiation of Planet Earth

*Today*

1. Evolution of the atmosphere

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#### Earth Differentiation: the Atmosphere

Interesting questions regarding the formation and evolution of Earth's atmosphere include:

- ✘ When did volatiles segregate from the silicate earth?
- ✘ How has the composition of Earth's gas envelope changed over geological time
- ✘ How and when did the present atmosphere-hydrosphere system form?

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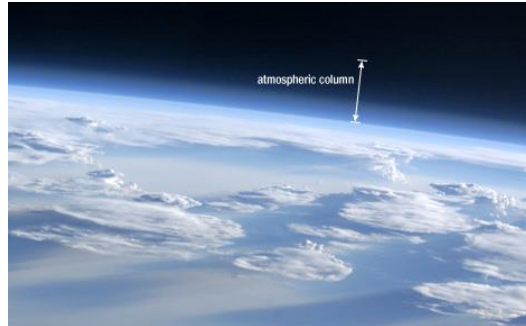
## Earth's atmosphere today

It is useful to review the features of our modern atmosphere, as a point of reference.

Our modern atmosphere:

- 78% N<sub>2</sub>, 21% O<sub>2</sub>, 0.93% Ar, 0.039% CO<sub>2</sub>, plus small amounts of other gases, including N, S, and other C species.
- physically and chemically stratified; for example, above and below the tropopause.

Most of what we think of as weather is caused by air movements within the lowest part of the atmosphere, the troposphere. This is also the part of the atmosphere that is most directly related to the hydrosphere.



ozonewatch.gsfc.nasa.gov

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## Earth's atmosphere today

It is useful to review the features of our modern atmosphere, as a point of reference.

- Water vapor from the hydrologic cycle does not travel freely above the tropopause because of a temperature inflection that causes significant crystallization of H<sub>2</sub>O to ice.

There is water above the tropopause but most of it is produced and destroyed through photochemical oxidation of methane in the stratosphere (and similar reactions)



View across the tropopause from a high flying research aircraft. Below are tropospheric clouds, above are rare nacreous clouds formed at the low temperatures of the tropopause and lower stratosphere. Imaged by Paul Newman of NASA Goddard Space Flight Center. <http://www.atoptics.co.uk/highsky/htrop.htm>



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## Earth's atmosphere today

The structure of our modern atmosphere is shown below. The tropopause is highlighted with an arrow:

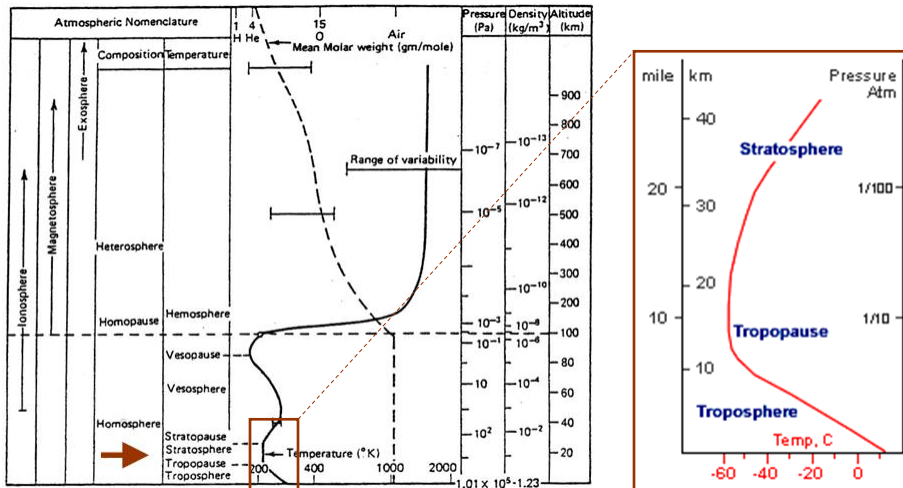


Figure 8.1 Structure and composition of the atmosphere.

Mason and Moore, *Principles of Geochemistry*, 4th ed

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## Composition of the modern atmosphere

The lower atmosphere is composed of:

- constituents that are constant in composition throughout
- naturally variable components. These reflect photochemical reactions (especially above the tropopause) and exchanges with the geosphere-biosphere-hydrosphere) below the tropopause:

- water vapor
- N and C species produced by biological and human activity on the earth's surface
- S species from volcanic, biologic and human sources
- O<sub>3</sub> from photochemical reactions and human activities
- very trace quantities of organic molecules of both natural and human origins.

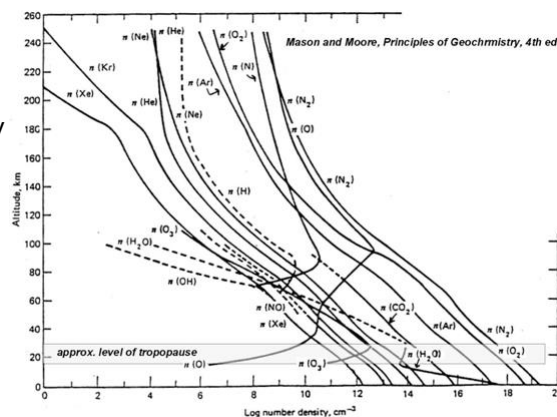


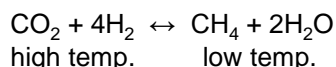
Figure 8.2 Vertical distribution of atmospheric constituents from surface to 250 km. (After Air Force Geophysics Research Directorate, 1960.)

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## Evolution of Earth's atmosphere

In the early stages of accretion, our **proto-atmosphere** very likely had **low  $E_H$**  because of the higher  $H_2$  abundance.

Probable gases were  **$CO_2$ ,  $N_2$ ,  $H_2O$ , Ar,** and **possibly  $NH_3$** . A potentially important equilibrium was



The extent to which this reaction occurred depends on the time-temperature path of accretion and on when the Earth lost most of its nebular  $H_2$ . This reaction is also affected by  $N_2$ - $NH_3$  equilibrium.

In any case, the **earliest atmosphere** was probably **at least somewhat reducing** and **dominated by C**, whereas now it has only **~0.039% C** and is oxidizing.

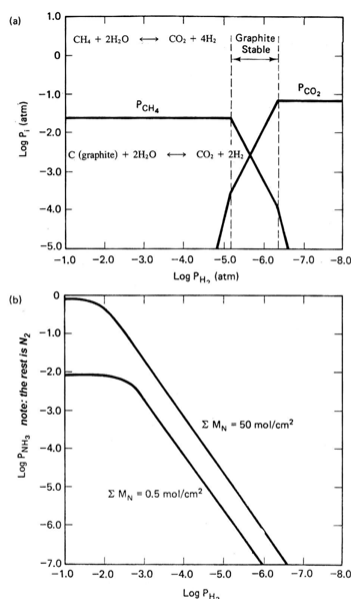


Figure 4.12 Equilibrium partial pressures of major carbon and nitrogen gases as functions of  $P_{H_2}$  at 25°C. (a)  $P_{CH_4}$  and  $P_{CO_2}$  calculated for a total atmospheric carbon concentration of 1.5 moles  $cm^{-2}$ ; (b)  $P_{H_2}$  calculated for two values of total nitrogen abundance. (After H. D. Holland, *The chemical evolution of the atmosphere and oceans*. Copyright 1984 by Princeton University Press. Reprinted with permission.)

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## Evolution of Earth's atmosphere

Early estimates suggested the primordial atmosphere was **poised at a pE** set by the **"QFI"** buffer (quartz-fayalite-iron);

i.e., near the  **$Fe^0/Fe^{2+}$**  couple.

Many **magmatic systems** are poised at or near the **"QFM"** (quartz-fayalite-magnetite) buffer; that is, near the  **$Fe^{2+}/Fe^{3+}$**  couple.

The relationship of  $O_2$  fugacity vs. T for these two reactions has been determined experimentally. (Recall that fugacity is a measure of pressure that includes a non-ideality correction, in the same way that aqueous activity is related to molarity.)

Using these buffers and estimates of total abundance for each element, we can predict what form the atmospheric gases will be in at each pE as a f(T). See next page for a sample calculation.

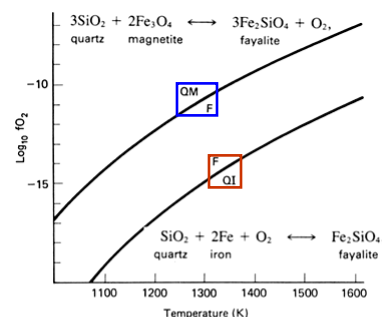


Figure 4.11 Calculated curves indicating the oxidation state of magmatic systems buffered by Quartz + Fayalite + Magnetite (QFM) or Quartz + Fayalite + Iron (QFI) as a function of temperature. The two curves are approximately four orders of magnitude apart over the temperature range for most volcanic events.

	QFM	QFI
$H_2O$	0.91	0.30
$H_2$	0.02	0.64
$CO_2$	0.057	0.0097
$CO$	0.0031	0.051
$SO_2$	0.0013	$2.0 \times 10^{-7}$
$H_2S$	$1.3 \times 10^{-5}$	0.0014
$N_2$	0.0018	0.0018
$O_2$	$3.4 \times 10^{-9}$	$4.0 \times 10^{-13}$
$CH_4$	$4.7 \times 10^{-14}$	$2.7 \times 10^{-7}$
$CO_2/CO$	18.4	0.19
$SO_2/H_2S$	100.0	$1.4 \times 10^{-4}$
$H_2O/H_2$	45.5	0.46

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Given the following simple conditions, let's calculate the gas content ( $P_i$  for each phase) of a closed system of magma and gas at equilibrium with the QFM buffer:

**Initial conditions:**

Magma temperature = 1100°K  
 Pressure ( $P_{tot}$ ) = 1 atm  
 C:H ratio = 0.05  
 Allowable gaseous species (for simplicity):  $O_2, H_2, H_2O, CO, CO_2$

We have 5 unknowns, so we need 5 equations for a unique solution. *see boxes*

To solve for the five unknowns, we must write five equations. Two of these follow directly from the bulk chemistry of the system. Because total pressure is 1.0 atm., we know that

**Conservation of mass equation**

$p_{H_2} + p_{H_2O} + p_{CO} + p_{CO_2} + p_{O_2} = 1.0.$

Because the atomic ratio C : H is 0.05, we also know that

**C to H ratio equation**

$(p_{CO} + p_{CO_2}) / (p_{H_2} + p_{H_2O}) = 0.1.$

The partial pressure of  $O_2$  is defined by the QFM buffer at the temperature specified. An empirical equation commonly used for this purpose

**$F_{O_2}$  with Temp. equation**

$$\log f_{O_2} = 9.00 - (25738/T),$$

where  $T$  is the temperature in Kelvins. In this example, then,

$f_{O_2} = 1.8 \times 10^{-10}.$

Assuming ideality, this is also the partial pressure of  $O_2$ , in atmospheres.

The final two equations are based on the stoichiometry of the gas species. From the potential reaction

**$CO_2$ -CO equilibrium equation**

$$2CO_2 \leftrightarrow 2CO + O_2,$$

we calculate that

$f_{CO_2} / f_{CO} = (f_{O_2} / K_e)^{1/2},$

in which  $K_e$  is the equilibrium constant for this reaction between carbon species. It has a value, under these conditions, of  $3.79 \times 10^{-13}$ . The only other independent chemical reaction that can be written is

**$H_2O$ - $H_2$  equilibrium equation**

$$2H_2O \leftrightarrow 2H_2 + O_2,$$

from which

$f_{H_2O} / f_{H_2} = (f_{O_2} / K_h)^{1/2}.$

The equilibrium constant,  $K_h$ , has the value of  $8.82 \times 10^{-14}$  at 1373 K.

**The equations can be solved simultaneously to yield**

 $P_{H_2} = 1.97 \times 10^{-2}$  atm  
 $P_{H_2O} = 0.89$  atm  
 $P_{CO} = 4.00 \times 10^{-3}$  atm  
 $P_{CO_2} = 8.70 \times 10^{-2}$  atm

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## Evolution of Earth's atmosphere

Today's atmosphere is **far more oxidizing**. This is both a result of and a key indicator of life, particularly **photosynthetic life**.

The compositions and magnitude of chemical exchanges between the atmosphere, biosphere, crust, and deep Earth have been modified considerably by biological evolution, and by climatic and tectonic cycles.

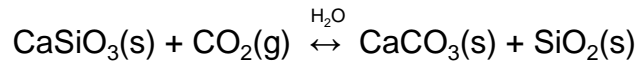
This caused the **transition** from a **somewhat reducing** to a **strongly oxidizing atmosphere**.

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## Evolution of Earth's atmosphere

Important events and processes that affected this **transition**:

1. Early loss of light elements and “blow off” of the proto-atmosphere.
2. Degassing from the planet’s interior.
3. Regulation of CO<sub>2</sub> by liquid H<sub>2</sub>O, allowing it to go into rocks via the *Urey reaction* (not storing CO<sub>2</sub> in rocks is a main reason why Venus so different from Earth):



4. Evolution of photosynthetic life and the buildup of atmospheric O<sub>2</sub> and O<sub>3</sub>.
5. Poising by the S<sup>2-</sup>/S<sup>4+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couples.

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## Evolution of Earth's atmosphere

Essentially, Earth's atmosphere went from one dominated by CO<sub>2</sub> to one dominated by O<sub>2</sub>. This is an older representation of the change.

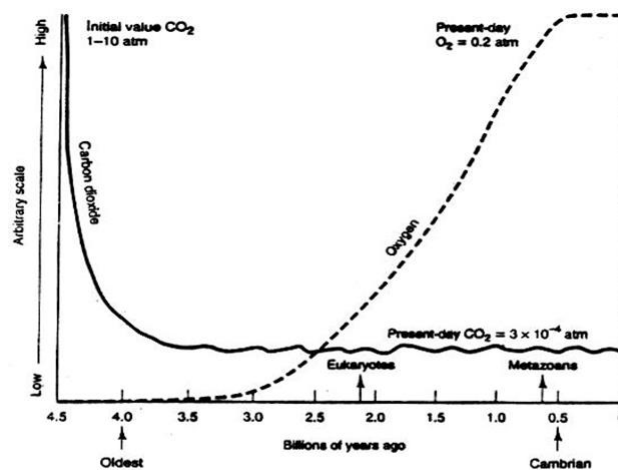
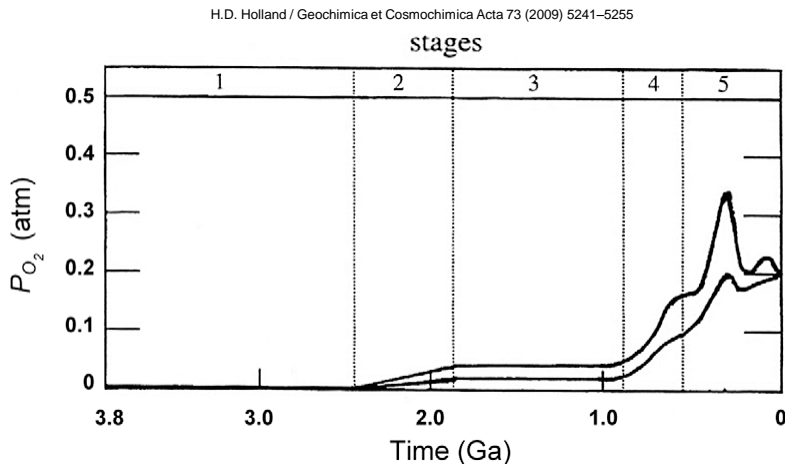


FIGURE 3-10 The history of oxygen and carbon dioxide in the atmosphere during Earth history.

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## Evolution of Earth's atmosphere

A more recent and speculative rendering of the history of O<sub>2</sub> accumulation in Earth's atmosphere.

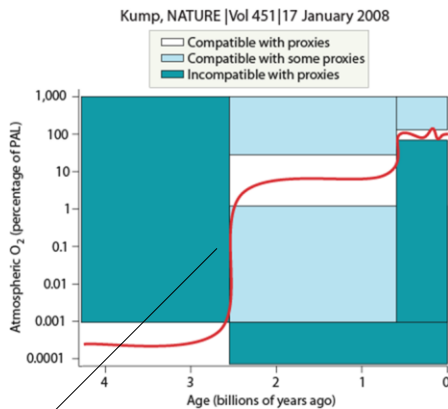


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## Evolution of Earth's atmosphere

The “current” view (Kump 2008) of atmospheric oxygen through time.

PAL = “present atmospheric level”



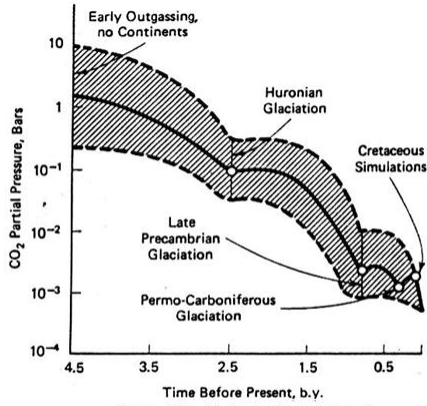
The great oxidation event

Rapid rise in O<sub>2</sub> between at about 2.5 Ga  
this rendering suggest a more sudden onset of O<sub>2</sub> change

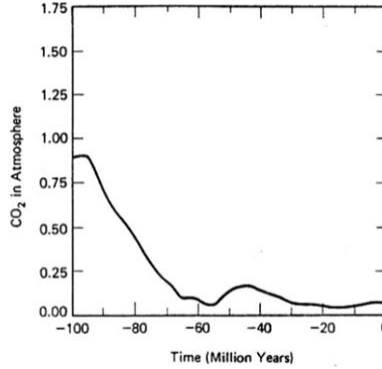
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## Evolution of Earth's atmosphere

At the same time, CO<sub>2</sub> has dropped many orders of magnitude

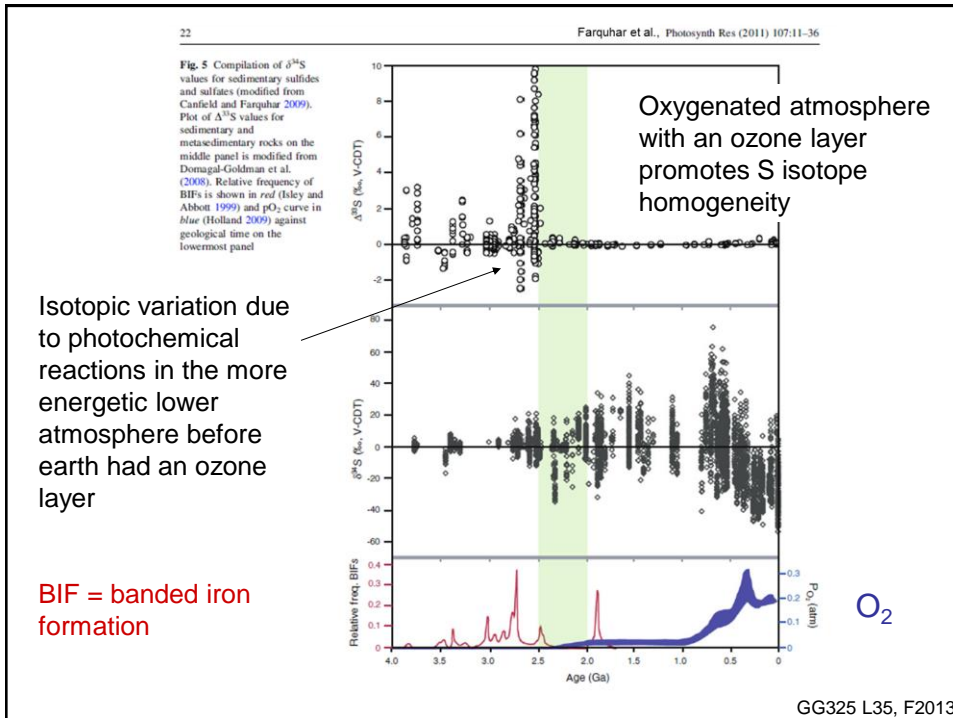


**Figure 4.13** Limits on the evolution of atmospheric CO<sub>2</sub>, inferred primarily from the greenhouse-supported temperatures necessary to avoid runaway glaciation. (Modified from Kasting 1986.)



**Figure 4.9** Variations in P<sub>CO<sub>2</sub></sub> during the Cenozoic, as calculated by the model of Berner et al. (1983, 1985). (After R. A. Berner, A. C. Lasaga, and R. M. Garrels, An improved geochemical model of atmospheric CO<sub>2</sub> fluctuations over the past 100 years. In *The carbon cycle and atmospheric CO<sub>2</sub>: Natural variations Archean to present*, ed. E. T. Sundquist and W. S. Broecker, 397–411. Monograph 32. Copyright 1985 by the American Geophysical Union. Reprinted with permission.)

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## Evolution of Earth's atmosphere

Taking inventory of our planetary volatiles requires looking to other parts of the rock record as well:

Table 4.1 Volatiles on the Earth<sup>a</sup>

Volatiles	Total Quantity (grams)	Atmosphere (grams)	Oceans (grams)	Sediments (grams)
H <sub>2</sub> O	1.6 × 10 <sup>24</sup>	1.7 × 10 <sup>19</sup> (0.001%)	1.4 × 10 <sup>24</sup> (88%)	1.9 × 10 <sup>23</sup> (12%)
CO <sub>2</sub>	2.4 × 10 <sup>23</sup>	2.5 × 10 <sup>18</sup> (0.001%)	0.4 × 10 <sup>20</sup> (0.06%)	2.4 × 10 <sup>23</sup> (99.9%)
N <sub>2</sub>	4.9 × 10 <sup>21</sup>	3.9 × 10 <sup>21</sup> (79.5%)	2.2 × 10 <sup>19</sup> (0.5%)	1.0 × 10 <sup>21</sup> (20%)
Cl	3.1 × 10 <sup>22</sup>	5.0 × 10 <sup>12</sup> (0%)	2.6 × 10 <sup>22</sup> (84%)	5.0 × 10 <sup>21</sup> (16%)
S	5.2 × 10 <sup>21</sup>	5.0 × 10 <sup>12</sup> (0%)	1.2 × 10 <sup>21</sup> (23%)	4.0 × 10 <sup>21</sup> (77%)

<sup>a</sup> The amounts are given as the mass of H<sub>2</sub>O, CO<sub>2</sub>, N (nitrogen-atom equivalents), Cl (chlorine-atom equivalents), or S (sulfur-atom equivalents).

<sup>a</sup>Source: J. C. G. Walker, *Evolution of the Atmosphere* (New York: Macmillan, 1977).

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## Evolution of Earth's atmosphere

The total inventory of volatiles in the atmosphere today shows that it is **significantly depleted in most gaseous elements** relative to the 90%-10% chondritic bulk-Earth model.

The atmosphere today is also **significantly less dense** than predicted by the 90%-10% chondritic bulk-Earth model.

Furthermore, volatile element **inventories “stored”** in the oceans, sediments, and rocks don't account for the difference.

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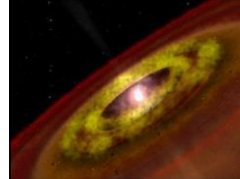
## Evolution of Earth's atmosphere

Most geochemists argue that the primordial atmosphere, or **Stage 1 atmosphere**, was removed (“**blown off**”) early in the planet's evolution.

This proto atmosphere was replaced by a secondary, or **Stage 2 atmosphere**, which subsequently evolved into our present one.

Primary causes of **stage 1 atmosphere blow-off** would have been

- late-stage giant impacts (the largest of which was apparently Theia)
- strong young star solar winds (T Tauri phase).



Artist's rendition of a T-Tauri star and proto-planetary disk – see Lecture 32

*Evidence for early atmospheric removal:*

- From accretion models, we expect **nitrogen to be 275-400 times as abundant as it actually is.**

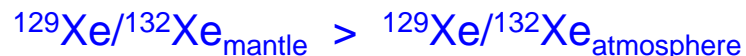
This implies that 99.6% to 99.8% of our early atmosphere was lost.

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## Evolution of Earth's atmosphere

*More evidence for early atmospheric removal*

- Another line of evidence for significant early loss of volatiles comes from xenon isotopes (discussed a few lectures ago).



This tells observation that some  $^{129}\text{I}$  ( $t_{1/2} = 15.7$  Myr), which is non-volatile and decays to  $^{129}\text{Xe}$ , was still “alive” in the mantle when most of the primordial atmosphere was removed.

Later, additional  $^{129}\text{Xe}$  outgassed from the mantle into the Stage 2 atmosphere.

(a little bit is still outgassing today).

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## Evolution of Earth's atmosphere

More evidence for early atmospheric removal

3. Argon is a rare gas, like Xe.

Once Ar is outgassed from the interior it stays in the atmosphere.

$^{40}\text{Ar}$  forms by radioactive decay of  $^{40}\text{K}$  ( $t_{1/2} = 1.25$  Gyr), whereas  $^{36}\text{Ar}$  is non-radiogenic.

$$^{40}\text{Ar}/^{36}\text{Ar}_{\text{mantle}} \gg ^{40}\text{Ar}/^{36}\text{Ar}_{\text{atmosphere}}$$

- The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio produced by nucleosynthesis is  $\sim 0.005$ .
- The Ar isotopic composition of today's atmosphere is  $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$ .
- The  $^{40}\text{Ar}/^{36}\text{Ar}$  coming from the mantle in volcanic systems today is 2000-5000.

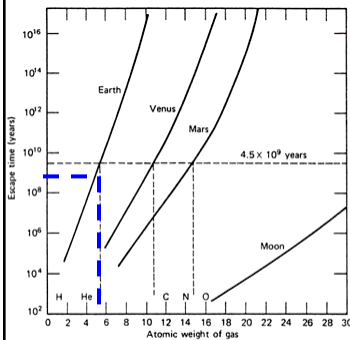
These values indicate **early loss of most of the Earth's  $^{36}\text{Ar}$** , before much  $^{40}\text{Ar}$  had built up by  $^{40}\text{K}$  decay and degassed from the interior.

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## Evolution of Earth's atmosphere

✂ How much **gas has been lost** after the blow-off of the Stage 1 atmosphere?

Gas escape to space is governed by the mass and kinetic energy of an atom or molecule, and the mass of the planet. One estimate of escape times versus mass for Earth, Mars, Venus and the Moon is discussed below:



Calculated effective time of escape of gases for earth, Venus, Mars and the moon. (After Jastrow and Rasool in *Introduction to Space Science*, W. N. Hess ed; Gordon and Breach, New York 1965, p 676.)

To escape the planet, a species must have sufficient energy to exceed the planet's gravitational pull.

The effective escape times of different gaseous species are calculated by comparing the number of gaseous atoms or molecules with sufficient velocity given the population distribution of gases at a given kinetic energy, to that required for escape.  $V_{\text{escape}}^2 = 2 \text{ Gm/R}$  (where G, M and R = Earth's gravitational field, mass, and radius, respectively)

The number of gas particles above  $V_{\text{escape}}$  has changed over Earth history since kinetic energy ( $= \frac{1}{2} mv^2$ ) is a function of temperature ( $\frac{3}{2} kT$ ) ( $m = \text{mass of the gas}$ ,  $v = \text{average velocity of gas particles}$ ,  $k = \text{Boltzman's constant}$ ,  $1.3807 \times 10^{-23} \text{ J}^\circ\text{K}$ )

$\frac{1}{2} mv^2 = \frac{3}{2} kT$ , so  $v = (\frac{3}{2} kT/m)^{1/2}$ , so  $v$  is proportional to  $T^{1/2}$  and  $(1/m)^{1/2}$

**The dashed horizontal line at the age of the solar system ( $4.55 \times 10^9$  yrs) intersects Earth's curve at mass - 5. Only species less massive than this ( $^2\text{H}$ ,  $^3\text{H}$ ,  $^3\text{He}$ ,  $^4\text{He}$ , and the mixed isotope  $\text{H}_2$  species) will have significantly escaped the Earth over its history.**

Venus, Mars and the Moon have seen more escape of more massive elements over this time period (Venus because it is closer to the sun and has more energetic atmospheric gas molecules and Mars and the Moon because they are cooler but smaller than Earth).

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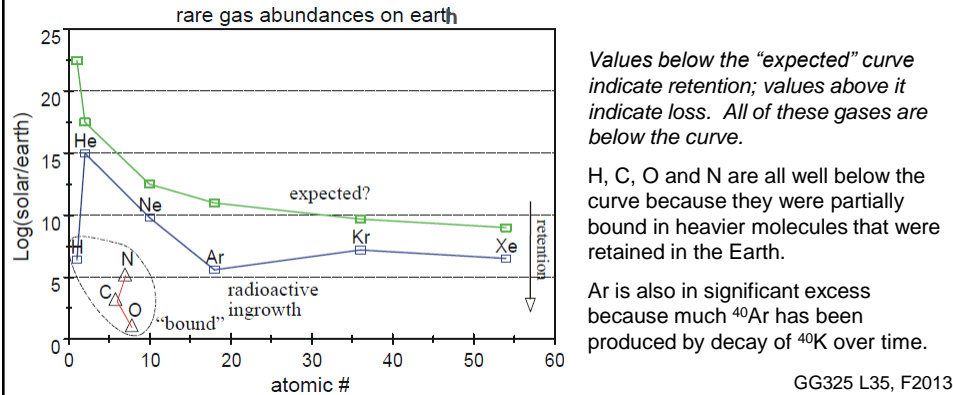
## Evolution of Earth's atmosphere

Temperatures may have been high very early in the evolution of the Stage 2 atmosphere, and some heavier gases may have been lost.

However, by at least 4 Ga sediments deposited from liquid H<sub>2</sub>O were being formed, which implies similar surface temperatures to today.

The pattern of rare-gas abundances below provides additional information.

The “expected” solar-to-Earth ratios are based on solar abundances, temperatures allowing liquid water within the first 0.2-0.3 Gyr of Earth history, and the expected rate of early degassing from estimates of accretion rate.



## Evolution of Earth's Stage 2 atmosphere

When liquid water first condensed on the Earth, surface rocks and the atmosphere must have had an  $E_H$  low enough to sustain Fe<sup>2+</sup>, because we *don't find evidence for significant Fe<sup>3+</sup> in early Archean rocks*. And because of the high abundance of iron in surface rocks, iron must have regulated the pE of the early atmosphere.

The oxidizing atmosphere developed later.

The primary abiotic O<sub>2</sub> source is photo-dissociation of water



This reaction produces only a small amount of O<sub>2</sub>, which must have gone into oxidizing Fe<sup>2+</sup> to Fe<sup>3+</sup> (and/or oxidizing other reduced chemicals) in the crust.

It's currently estimated that the prebiotic atmosphere had pO<sub>2</sub> < 10<sup>-12</sup> atm (and pCO<sub>2</sub> > 1 atm).

The main source of O<sub>2</sub> is photosynthesis. Once photosynthesizing organisms evolved (i.e., cyanobacteria or blue-green algae) and began producing significant amounts of O<sub>2</sub>, Fe<sup>2+</sup> in surface rocks and waters was oxidized and pE<sub>atm</sub> began to slowly increase.

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## Evolution of Earth's Stage 2 atmosphere

- Permian = trees ●
- Cambrian explosion ●
- Ozone layer and Multi-cellular life ●
- Paleosols with Fe ●
- BIFs ●
- $\Delta S^{34}$  variation stops ●

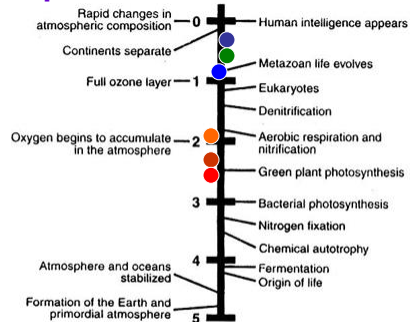


Figure 4.12 The coevolution of life and the environment to the present time. Key evolutionary advances are indicated to the right of the time line, and critical developments in the physical environment are on the left. (Chronology from J. C. G. Walker, *Evolution of the Atmosphere* [New York: Macmillan, 1977])

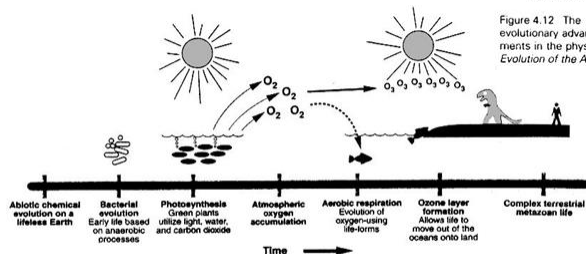


Figure 4.6 Milestones in the coevolution of life and the environment. Living organisms have become increasingly complex over time, and biological processes have had a major impact on the composition of the atmosphere. Evolution, in turn, has responded to changes in the atmosphere's composition by producing life-forms that could utilize atmospheric gases.

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## Evolution of Earth's Stage 2 atmosphere – the narrative

3.8 Ga: oldest unrefuted evidence for life (from C isotopes in biogenic apatite).

3.5 Ga: oldest fossils (bacteria in Australian sediments). Good evidence exists for cyanobacteria by at least 3.0 Ga (stromatolites –see *modern example from Australia in image at right*); large-scale  $O_2$  production underway. Life was likely restricted to aquatic forms, because of intense UV radiation (which water absorbs) reaching the surface.



3-2.7 Ga: variations in S isotopes – early  $S^{-2}/S^{+4}$  ● posing of atmosphere/hydrosphere, followed by Fe II/Fe III poisoning, when most banded iron ● formations (BIFs) are deposited.



2.6-2.3 Ga: globally significant deposits of BIFs and other Fe-rich sandstones, which also contain significant concentrations of Mn.

Both images from [http://www.amnh.org/learn/resources/earth\\_resource1.php](http://www.amnh.org/learn/resources/earth_resource1.php)

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## Evolution of Earth's Stage 2 atmosphere – the narrative

2.3 Ga: BIFs no longer forming in large quantities;  $pO_2/pCO_2 \approx 10^{-5}$ .

Atmospheric  $O_2$  must have reached about 0.5% of the modern concentration by this time, in order for dissolved  $Fe^{2+}$  and  $Mn^{2+}$  to become insoluble and be deposited regularly in sediments. U concentrations in sedimentary rocks also went down as pE rose;  $U^{4+}$  (insoluble) converted to  $U^{6+}$  (soluble).

2.0 Ga and later: paleosols (fossil soils) now contain significant Fe (all as  $Fe^{+3}$ ). Older soils had essentially no Fe because it was leached away as soluble  $Fe^{2+}$ . ●

Paleosol preserved between two lava flows on the Isle of Skye, Scotland  
<http://www.uwgb.edu/dutchs/EarthSC202Slides/soilslid.htm>



It took another ~1.3 Gyr for multicellular life to evolve near the end of the Proterozoic Eon of the Precambrian (at about 700 Ma).

Probably by about 1 Ga, the protective stratospheric ozone layer probably started building up, allowing more complex life forms to begin to evolve. ●

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## Evolution of Earth's Stage 2 atmosphere

$O_2$  continued to build up, to ~5% of the modern value by ~545 Ma, coinciding with the “Cambrian explosion” of higher organisms having differentiated cells.

The continued buildup of the  $O_3$  layer allowed land plants and animals to begin to evolve. By about 430 Ma, things were starting to look pretty familiar (from our perspective). ●

By the end of the Paleozoic (Permian), forests had covered the land and then been buried, giving rise to enormous coal deposits in the Carboniferous. ●

$O_2$  continued to increase. It may even have been **several percent higher** in the Carboniferous and Cretaceous atmosphere than today.

$CO_2$  levels fluctuated throughout, generally **dropping**, from the controls we've already discussed.



Permian forest, news.discovery.com

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