12

Evolution of Atmospheric Composition and Pressure

The thickness of the Earth's atmosphere is about 300 miles (480 kilometers). Due to gravity, most of the mass of the total atmosphere lies within a layer ≈8 miles (16 km) thick over the Earth's surface. The lowest layer of the Earth's atmosphere is referred to as the troposphere. As described in the earlier chapters, the Earth's atmosphere composition and pressure have changed over time. The components of today's atmosphere are listed in Table 12.1. Air pressure decreases with altitude because of gravity as shown in Table 12.2. At sea level, the air pressure is ≈14.7 pounds per square inch (1 kilogram per square centimeter). At 10,000 feet (≈3 km), the air pressure is much lower, 10 lb/in^2 or psi (0.7 kg per square cm).

Partial Pressure of Atmospheric Gases

The total pressure of the Earth's atmosphere is a summation of the partial pressures of all the gases that make up the atmosphere. These primarily include nitrogen, oxygen, argon, carbon dioxide, methane and water vapor (see Table 12.1). A plot of the historic evolution of the Earth's atmosphere

Table 12.1 Composition of Earth's current dry atmosphere. (Data from Sflps, 2017.)

Component	Symbol	Percent by volume	Mixing ratio	Concentration, PPM
Nitrogen	n_2	78.084%	0.78	780.840.0
Oxygen	o_2	20.945%	0.209	209.460.0
Argon	Ar	0.934	0.00934	9,340.0
Carbon dioxide	CO_2	0.036	0.00036	360.0
Neon	Ne	0.00182	0.0000182	18.2
Helium	He	0.000524	0.0000052	5.24
Methane	ch_4	0.00015	0.0000015	1.5
Krypton	Kr	0.000114	0.00000114	1.14
Hydrogen	H_2	0.00005	0.0000005	0.5

Table 12.2 Barometric pressure at various altitudes (elevations).

Altitude, ft.	Barometric pressure, mm. Hg.
O (sea level)	760
5000	632
8,000	570
10.000	529
20,000	350
40.000	140
60,000	50

composition and pressure, in the absence of nitrogen bacterial consumption, is presented in Figure 12.1.

Today's atmospheric pressure is shown in Table 12.2. The partial pressure of each gas component is defined, as the pressure that would be excreted by the molecules of gas × if all the other gases were removed from the mixture of atmospheric gases. Because many of the concentrations of the gases have a low partial pressure, one can use Dalton's ideal gas law, which states that the partial pressure (p_x) of gas × is related to the total pressure, p_t = atmosphere, by the mixing ratio, C_X:

$$p_X = C_X p_t , \qquad \text{(Eq. 12.1)}$$

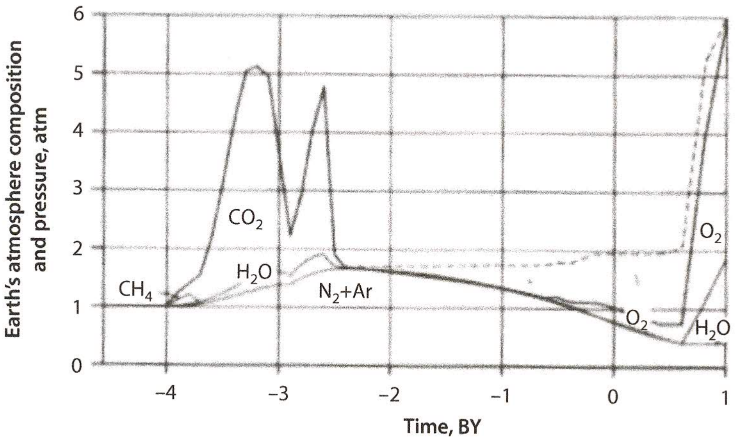

Figure 12.1 Earth's atmosphere composition and pressure evolution. The dashed line is the atmospheric pressure in the absence of bacterial consumption of nitrogen.

Or, the partial pressure (p_x) is equal to the total pressure times the mole fraction, y_x, of a particular gas in a mixture of gases:

$$p_x = p_t\, y_x \qquad \text{(Eq. 12.2)}$$

The value of the total atmospheric pressure, p_t, is presented in Table 12.2 at various altitudes. The partial pressure of a gas is a measure of the frequency of collisions of gas molecules with surfaces or other molecules.

As noted in Figure 5.1, when the Earth was formed from the debris of a nebula, its atmosphere contained very low amounts of inert nitrogen and just traces of noble gases but higher quantities of hydrogen and helium. The Earth's atmospheric pressure at that time did not exceed 1 mbar. During the Archaean time, the primordial atmosphere contained none of the chemically active gases (e.g., CO_2, CO, O_2, or H_2O) as all these components were rapidly absorbed by the regolith covering the surface of the Earth. Due to the high surface temperatures, the hydrogen and helium molecules had an escape velocity adequate to escape the Earth's atmosphere.

The Earth's degassing of the mantle began during the Early Archaean time. The Earth's atmospheric pressure comprised the partial pressures of carbon dioxide, nitrogen, and methane. At that time, the carbon dioxide content in the atmosphere was increasing due to the CO_2 reduction of iron (see Figure 5.1). The atmosphere was substantially reducing and consisted of carbon dioxide, nitrogen, and methane. Beginning at about 3.5 BY ago, after a significant rise in the atmosphere's average temperature (see Chapter 14), the atmosphere's carbon dioxide-nitrogen composition was amended by the partial pressure of water vapor. After the methane dissociation (≈3.8 BY ago), the Earth's atmosphere became a neutral carbon dioxide-nitrogen gas-shell.

The nitrogen partial pressure noticeably increased in the Late Archaean time due to nitrogen degassing from the mantle. The carbon dioxide pressure began declining at the end of the Archaean time, because the atmospheric carbon dioxide was intensely being bonded within carbonates. After the core separation and the formation of the Earth's crustal serpentine layer (see Figure 5.15), which emerged because of the severe decline in tectonic activity, almost the entire carbon dioxide in the atmosphere was bonded in carbonate rocks.

During the Proterozoic time, the Earth's atmosphere became almost purely nitrogen with minute admixture of argon and methane (see Figure 12.1). Nitrogen's partial pressure may have reached 1.4 to 1.5 atm in the Early Proterozoic time. Beginning in the Middle Proterozoic time, the Earth's atmospheric pressure began to decline noticeably due to the activity of nitrogen-consuming bacteria. Simultaneously, in the Late Riphean, oxygen started to accumulate rapidly in the Earth's atmosphere, especially after a total disappearance of the metallic iron from the Precambrian mantle.

During the Phanerozoic time, nitrogen's partial pressure continued to decline, although in Paleozoic and Mesozoic it was amply compensated by the accelerated accumulation of biogenic oxygen. Upon evolution of the flowering plants, which were the major oxygen generators at the end Mesozoic, the Earth's atmosphere's pressure reached ≈230 mbar. Oxygen together with nitrogen continued to increase the atmospheric pressure until it reached ≈1 atm. Later, in the Cenozoic, Earth's atmospheric pressure began dropping again. This atmospheric pressure decline resulted in the cooling of the Earth's climate. This may have noticeably affected the activity of the nitrogen-consuming bacteria, which, in turn, resulted in a decreased nitrogen partial pressure.

Nitrogen-consuming bacteria have played a positive role in the evolution of the Earth's climate, creating favorable conditions for the evolution of life on Earth. Without the bacteria and the production of nitrogen, the current atmospheric pressure would be approximately 2 atm and the resulting average Earth's surface temperature would be over 180 °C at the equator. The latter is above the coagulation temperature of some vitally important proteins. It is likely that favorable conditions for life may have been present only on the mountaintops at high latitudes (lower temperatures). Vitally important oxygen could not have accumulated in sufficient amounts under such extreme conditions. In fact, if not for nitrogen removal from the atmosphere, the Earth would be presently (as in Archaean) populated only by the thermophilic bacteria and maybe the primitive multicellular organisms.

In the future, there will be a drastic oxygen partial pressure increase in 600 MY. This will be due to abiogenic oxygen degassing, as a result of the core separation process after the complete oxidation of the mantle iron to the stoichiometry. At that time the atmospheric pressure will rapidly rise and will exceed 10 atm due to the rise of oxygen content and partial pressure increase of the Earth's atmosphere.

Using the derived atmospheric composition and pressure, and the earlier proposed adiabatic theory of the greenhouse effect (Sorokhtin, 2001), it is possible to calculate the temperature parameters of the former, present, and future Earth's climates using Eq. 2.26.

Figure 12.1 was prepared, estimating the total atmospheric pressure and its varying content of components over geologic time. A sharp increase in the oxygen partial pressure in the future (≈600 MY), due to the increase in free abiogenic oxygen (gas not produced by the action of living organisms) from the Earth's mantle degassing process (Sorokhtin and Uskakov, 2002). This increase in free oxygen is the result of reducing the silicate iron oxide:

$$2\mathrm{FeO} \rightarrow \mathrm{Fe} \cdot \mathrm{FeO} + \mathrm{O}. \qquad \text{(Eq. 12.1)}$$

The released oxygen from this reaction, under high pressure and release of the compression energy (due to a smaller volume of the magnetite) again combines with FeO, forming the magnetite component of the mantle:

$$3\mathrm{FeO} + \mathrm{O} \rightarrow \mathrm{Fe_3O_4} + 76.48\ \mathrm{kcal/mole}. \qquad \text{(Eq. 12.2)}$$

After a total oxidation of the mantle iron silicate to magnetite formation, of the Earth's core matter will have to be accompanied by the release of free oxygen:

$$2\mathrm{Fe_3O_4} \rightarrow 3\mathrm{Fe} \cdot \mathrm{FeO} + 5\mathrm{O}. \qquad \text{(Eq. 12.3)}$$

As a result, in the future, additional free oxygen will enter the atmosphere, increasing the oxygen content as indicated in Figure 12.1. The partial pressure of oxygen will increase above 10 atm as a direct result of this additional oxygen influx. Eq. 2.26 indicates that this increase in pressure will raise the Earth's surface temperature above 180 °C. The Earth would be similar to the planet Venus. After evaporation of the ocean water, the atmospheric pressure will rise further and the Earth's temperature will exceed 600 °C. Surface temperatures of this magnitude will evaporate the oceans and destroy all life on the Earth. It should be noted that the current surface temperature on Venus is 460 °C, which is cooler than that of our future Earth, as it has a much higher carbon dioxide content in its atmosphere.