7

Development of Free Oxygen in Earth's Atmosphere

Oxygen

One fifth of the Earth's atmosphere is made up of oxygen, which is the third most abundant element in the universe by mass. The element oxygen has an atomic number of eight and is the 8^{th} element on the Periodic table. At normal pressure and temperature, the molecules of oxygen can bond to form a dioxide (O_2) which is a colorless gas that composes about 21% of today's atmosphere. Oxygen is the most reactive of the non-metallic elements, a member of the chalcogen group on the periodic table and readily forms compounds with elements other than the inert elements, i.e., helium or neon (Soft schools, 2017).

Today, the movement of oxygen can be seen in the oxygen cycle (Figure 7.1) within its three main reservoirs, the: (1) atmosphere, (2) biosphere (biological matter) and (3) lithosphere (Earth's crust) (CMU, 2003). The form of oxygen in the atmosphere is the gas, free oxygen (O_2). In the other two reservoirs, oxygen is bonded with either organic or inorganic material.

Table 7.1 lists the capacity for storage, the flux in/out and residence time for the three major reservoirs of free oxygen. The lithosphere, shown in

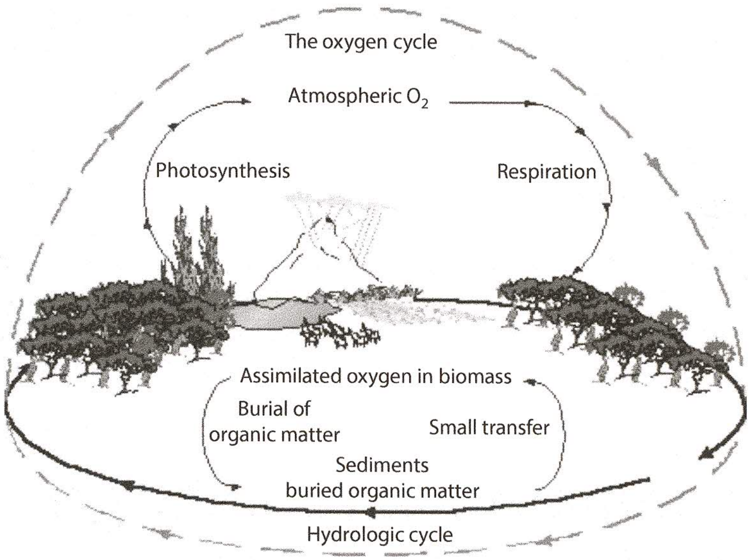

Figure 7.1 Today's oxygen cycle showing three main reservoirs of storage for oxygen: (1) atmosphere, (2) biological, and (3) Earth's crust. (After CMU, 2003.)

Table 7.1 Major reservoirs of oxygen involved in the oxygen cycle. (Data based primarily on estimates from (Walker, J. C. G.; in: Wikipedia, 2017))

Reservoirs	Capacity	Flux in/out, Kg O_2/year	Residence time, years
Atmosphere	1.4×10^{18}	3×10^{14}	4500
Biosphere	1.6×10^{16}	3×10^{14}	50
Lithosphere	2.9×10^{14}	6×10^{14}	500×10^{6}

Table 7.1, is the largest source of free oxygen. Today, approximately 99.5% of the Earth's oxygen is bound with silicate and oxide minerals. Only a small portion of oxygen is found as free oxygen to the biosphere (0.01%) and atmosphere (0.36%) (Wikipedia, 2017).

History of Free Oxygen in Earth's Atmosphere

As a free gas in the atmosphere, oxygen has only been present for the past 2.3 to 2.4 BY. The development of free oxygen in the Earth's atmosphere first appeared ≈2.5 BY ago (Figure 7.2). The correlation by Govindjee and

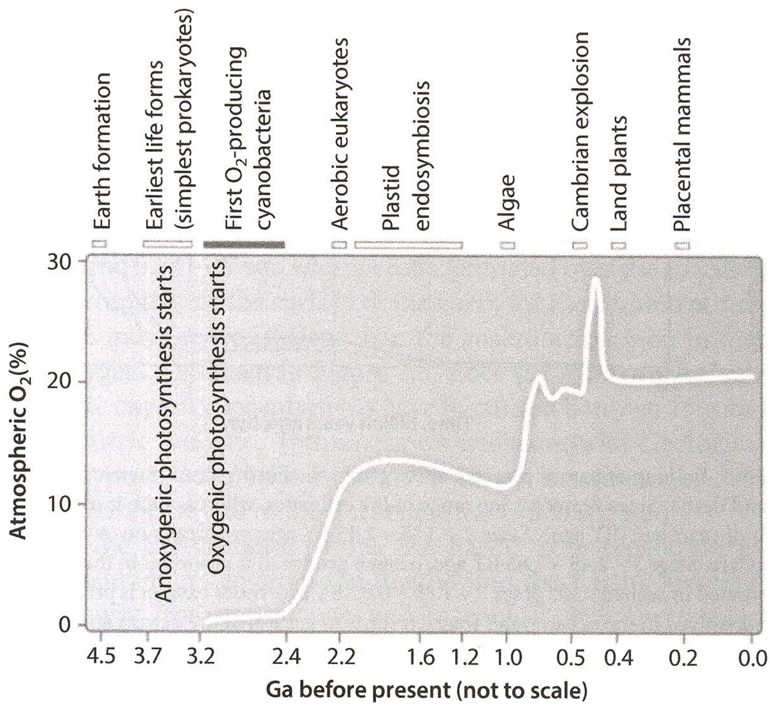

Figure 7.2 Development of free oxygen in the atmosphere. (After Govindjee and Shevela, 2011.)

Shevela (2011) estimated percent free oxygen concentration changes in the atmosphere with the major evolutionary events on the Earth is based on data presented by Falkowski (2006; 2011), Tomitani *et al.* (2006), Kump (2008), Blankenship (2002; 2010), and Hohmann-Marriott and Blankenship (2011). Uncertainties of the events in the evolution of life have been depicted with bars. There are several hypotheses as to when oxygenic photosynthesis was first developed by primitive cyanobacteria-like organisms. Govindjee and Shevela (2011) have summarized the currently available data and depict (by a black bar) that the first cyanobacteria likely evolved as early as 3.2 BY ago or as late as 2.4 BY ago.

The history of free oxygen in Earth's atmosphere can be divided into several phases or stages as shown in Figure 7.3: (1) *Stage 1*—there was little if any free oxygen gas, O_2, in Earth's atmosphere during the Hadean and early Archean times in significant quantities, until the beginning of the Proterozoic time. (2) *Stage 2*—Early in the Proterozoic time there was still little free oxygen in either the atmosphere or dissolved in the oceans; however, the percentage of oxygen increased slightly due to anaerobic bacterial

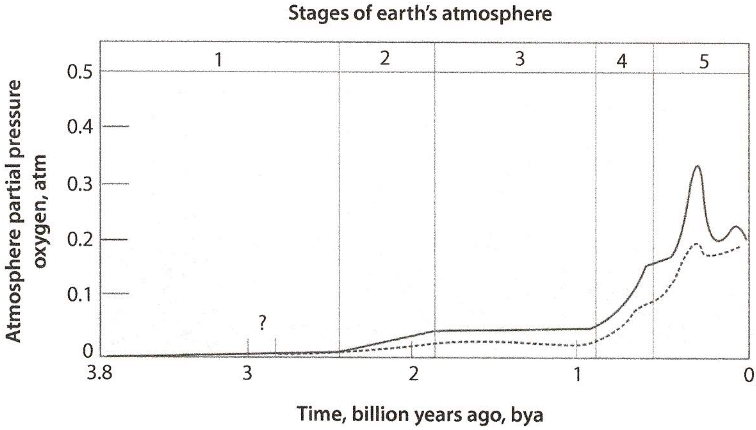

Figure 7.3 Buildup of partial pressure of oxygen in the Earth's atmosphere over time. Solid and dashed lines represent the range of the estimates, whereas time is measured in billions of years ago (BY ago). *Stage-1* – 3.85 – 2.45 BY ago, practically no oxygen in the atmosphere. *Stage 2* – 2.45 – 1.85 BY ago, oxygen produced is absorbed in the oceans and incorporated in seabed rock. *Stage 3* – 1.85 – 0.85 BY ago: more oxygen is produced than can be dissolved in the ocean water (oxygen starts to gas out of the oceans and is absorbed by the land surfaces and enriches the Earth's atmosphere). *Stages* 4 and 5 – 0.85 BY ago – today, oxygen enriches the atmosphere. (Modified after Oxygenation-atm.svg: Heinrich D. Holland derivative work; in: Wikipedia, 2017, https://en.wikipedia.org/wiki/Atmosphere_of_Earth.)

action. (3) *Stage 3*—as a result of the increase of *photosynthetic prokaryotic* organisms in the oceans, bacteria living in the ocean waters produced more free oxygen, which was released as dissolved gas in the water, than could chemically form oxides (Much of this produced free oxygen by the bacteria was removed chemically by oxidation of metals, most notably iron.) Today, these oxidized iron deposits are found in the form of banded iron oceanic sediments on the ocean floor. The excess free oxygen that was not expended in oxidation exceeded the gas solubility of the ocean water and escaped into the Earth's atmosphere. By the mid-Proterozoic time, oxygen began to appear in the Earth's atmosphere in small quantities as shown in Figure 7.3. *Stages 4 and 5,* the development of plants, during the Phanerozoic time, significantly increased the percentage of free oxygen in the atmosphere (first in *Stage 4* by plants within the ocean and later in *Stage 5* when plants developed on dry land). The additional oxygen, produced by bacteria and plants, injected enough free oxygen into the ocean and atmosphere to begin killing off most of the anaerobic bacteria (Wikipedia, 2017).

During the Pre-Cambrian time (Figure 7.3, *Stage 4*), prior to ≈1.9 BY ago, the production of oxygen by the anaerobic bacteria was less than that of the aerobic bacteria and plants. The generation of free oxygen during this era was primarily the result of generation of oxygen by *cyanobacteria* and *microalgae.* In the global oceans, there was an active absorption of oxygen by iron. The concentrations of free oxygen in the Earth's atmosphere were less than 10% of today's concentrations and appeared to have fluctuated greatly. Free oxygen even may have disappeared from the atmosphere again around 1.9 BY ago. The presence of free oxygen in the Earth's atmosphere around 0.541 BY ago when aerobic prevailed over the anaerobic life. New opportunities on the surface of the Earth for the aerobic metabolism made them much more efficient than the anaerobic bacteria in the presence of oxygen. As shown in Figure 7.3, since the start of the Cambrian, atmospheric oxygen concentrations have fluctuated between 15% and 35% of atmospheric volume. (https://en.wikipedia.org/wiki/Geological_history_of_oxygen - cite_note-Berner1999-10) A maximum of 35% was reached towards the end of the Carboniferous (≈300 BY ago).

During the Pre-Cambrian time, the Earth's core separation process iron gradually migrated from the mantle into the Earth's growing core. Simultaneously iron moved into and in contact with the hydrosphere through the oceanic rift zones. There, in the presence of carbon dioxide dissolved in the ocean water, oxygen was distributed throughout the entire ocean in the form of bicarbonate:

$$4Fe + 2H_2O + CO_2 \rightarrow 4FeO + CH_4 + 41.8 \text{ kcal/mole} \qquad \text{(Eq. 7.1)}$$

$$FeO + 2CO_2 + H_2O \rightarrow Fe(HCO_3)_2 \qquad \text{(Eq. 7.2)}$$

Due to the metabolism of some ferro-bacteria species, hematite could have been converted to magnetite (F_3O_4) which later was converted into many of the unique deposits of Pre-Cambrian Jaspillites.

The evolution of the oxygen partial pressure in the Earth's atmosphere over the past 4.5 BY is presented in Figure 7.4. This partial pressure curve of oxygen in Earth's atmosphere is directly related to the types of plant biogenic and bacterial organisms and their oxygen release rate. Figure 7.5 shows the atmospheric free oxygen partial pressure of oxygen for the past 1 BY (Pre-Cambrian to Present). Prior to the appearance of dry land vegetation, the free oxygen partial pressure was proportional with the ocean-water mass. Oxygen absorption had to be also proportional with the iron ore deposits earlier estimated by Sorokhtin (2004); Sorokhtin and Ushakov (2002). Figure 7.6 shows the total rate of iron-ore formation accumulation over the last 4.5 BY.

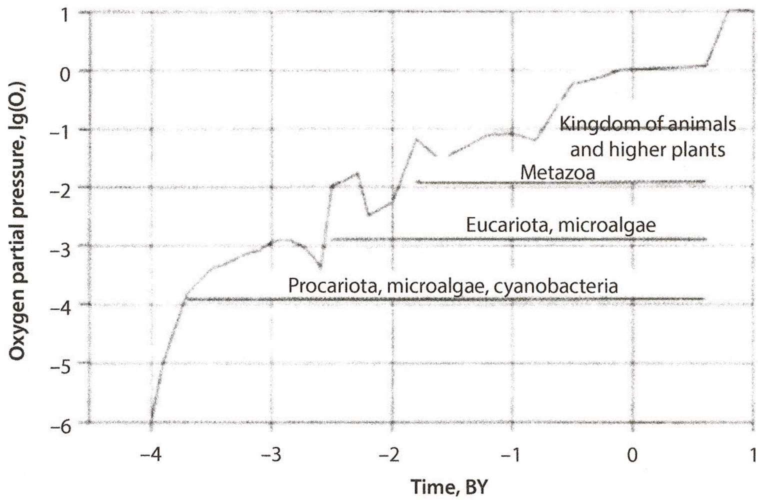

Figure 7.4 Oxygen partial pressure evolution in the Earth's atmosphere (logarithmic scale). In Pre-Cambrian time, oxygen was generated only by the oceanic biota. In the Phanerozoic time additional oxygen was generated by dry–land vegetation. It is assumed that oxygen generation by Archaean prokaryotes (*cyanobacteria*) was by one order of magnitude lower than by Proterozoic *eukaryote* microalgae.

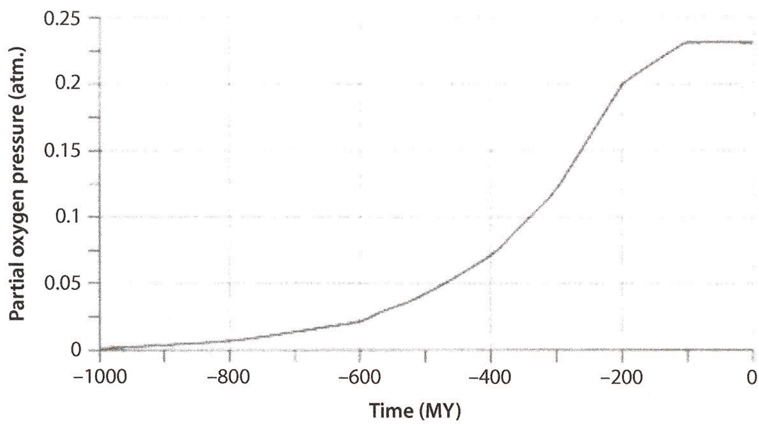

Figure 7.5 Atmospheric free oxygen partial pressure distribution over the last 1 BY (the present-day oxygen partial-pressure is 0.2315 atm.). (After Sorokhtin *et al.*, 2011, figure 12.10, p. 453.)

The biogenic oxygen accumulation in the Earth's atmosphere can be estimated by use of the following relationship:

$$p(O_2) = \frac{aM_{wo}}{b\text{Fe} + c} + p(O_2)_{cont}, \qquad \text{(Eq. 7.3)}$$

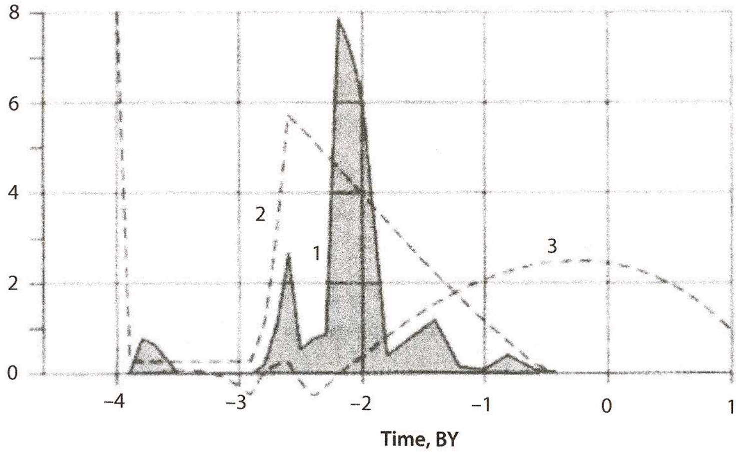

Figure 7.6 Theoretical accumulation rate of the Pre-Cambrian iron-ore formations. *Curve 1* – Total rate of iron ore formation, 10^9 t/year. *Curve 2* – Metallic iron concentration in the convecting mantle, %. *Curve 3* – Ocean surface position relative to the average standing level of mid-oceanic range ridges, km.

where M_{wo} is the water mass in the ocean (see Figure 4.11); Fe is the iron ore accumulation rate (see Figure 7.6); $p(O_2)_{cont}$ is the contribution by dry-land vegetation to the total oxygen partial pressure (in this estimate it was assumed that $p(O_2)_{cont} \approx 0.1$ atm.); factors *a*, *b* and *c* are selected so that the oxygen partial pressure in today's atmosphere would be ≈0.231 atm and for the atmosphere of 600 MY ago would have been lower by one order of the magnitude: ≈0.0231 atm. Using Eq. 7.3 (the logarithmic scale) enables comparison of the major stages in the evolution of Earth's biota as presented in Figure 7.7 (microfossils) and Figure 7.8 (tree of life).

Figure 7.6 demonstrates that every epoch of ferric deposition in the Pre-Cambrian corresponds to an oxygen partial pressure minimum. This can be explained when the oxidized iron is an active oxygen absorber. Also, oxygen partial pressure evolution can be compared with the major stages of the evolution of life on Earth as shown in Figures 7.7 and 7.8. New forms of life on the Earth have emerged following an increase in the atmospheric free oxygen partial pressure, i.e., after the end of the period accumulation of mass iron ore deposits. It should be noted that a change from *thermophilic prokaryote* to more *cryophiles eukaryote* microorganisms likely occurred due to substantial climate cooling in the Early Proterozoic.

As metallic iron migrated from the Pre-Cambrian mantle and migrated toward the Earth's core, biogenic oxygen began accumulating in the Earth's atmosphere as shown in Figure 7.4; this led to a significant restructuring of the entire Earth's biota and emergence of higher life forms (Sorokhtin

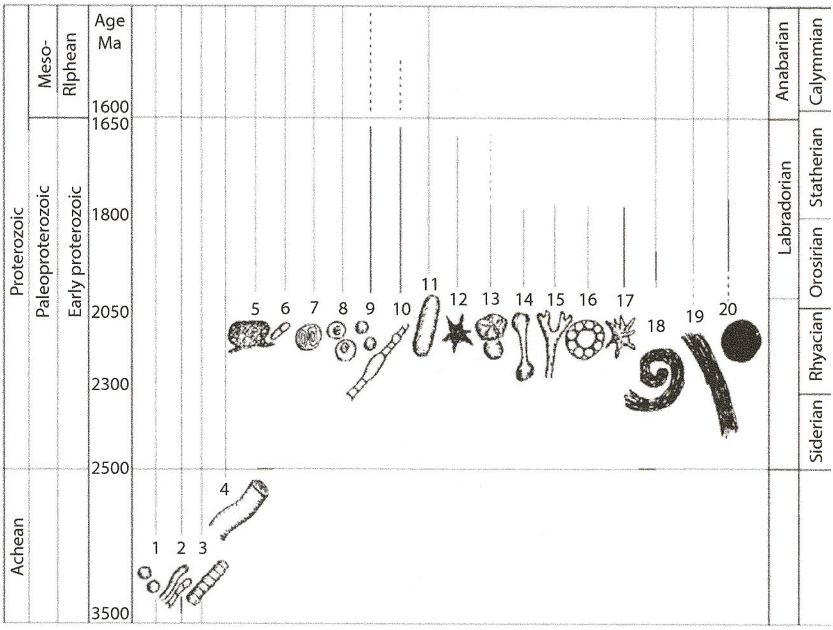

Figure 7.7 Major microfossil remains distribution in the Archaean and Early Proterozoic time (Semikhatov *et al.*, 1999). Common in the Archaean were mostly singular globular and filamentary nanobacteria (1, 2), trichomes and (3) possibly cyanobacteria filaments (4). The diversity of Early Proterozoic microfossils extends from cyanobacteria (4); (5–7), coccoid forms (8,9), trichomes (10) to impressions of large and morphologically complex (11–17), spiral (18), tape-like (19), round and globular (20) forms. (Sorokhtin *et al.*, 2011, figure 15.3, p. 533.)

and Ushakov, 2002). Figure 7.7 illustrates many of the changes in the major microfossil record in the Archaean and Early Proterozoic Eons. The increase in the free oxygen atmospheric partial pressure above 30 mbar was followed literally by an explosion in life's biota variety at the beginning of the eon. This period is often referred to as the *Cambrian Explosion*. It was a time that the skeletal biotic forms and most major types of existing life emerged (Figure 7.8). The emergence and bloom of higher life forms on Earth appears to have been facilitated by a 20 °C decline of planet's average near-surface temperature as supported by Eq. 2.26 and is thus related to a change in the Earth's atmospheric pressure.

The growth in the oxygen partial pressure in Late Riphaean and Phanerozoic (especially in the Mesozoic) was mostly compensated for by the decline, at the same time interval, of nitrogen's partial pressure. After the broad evolution of flowering plants (the major oxygen "manufacturers" at the end Mesozoic), the atmospheric oxygen partial pressure reached

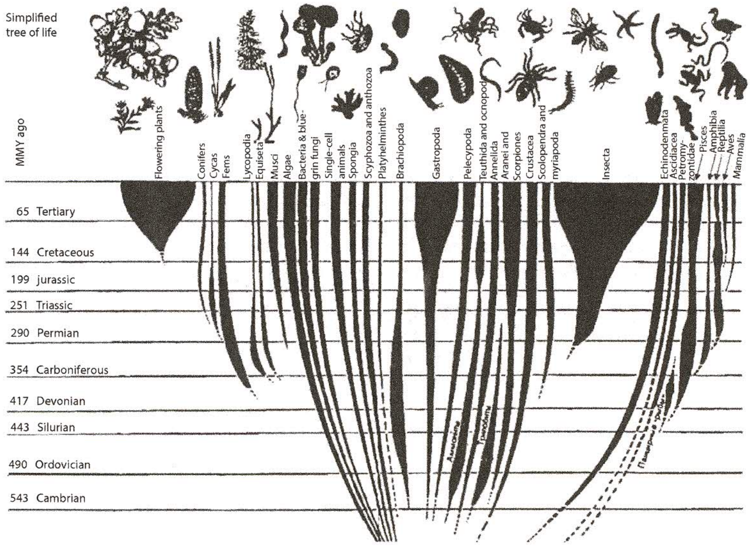

Figure 7.8 "Tree of life". The evolution of life at the Proterozoic/Phanerozoic time boundary was like a biological explosion. (Attenborough, D., *Life on Earth: A Natural History* (1984); in: Sorokhtin *et al.*, 2011, fig. 15-4, p. 534.)

its maximum value and even temporarily exceeded the declining nitrogen partial pressure. However, the growth of the oxygen partial pressure could not be unlimited as its growth was controlled by negative feedback, substantially stabilizing the free oxygen partial-pressure in the Earth's atmosphere. Among the feedback items was the rotting of organic remains and forest fires, which bonded the atmospheric free oxygen to carbon, forming carbon dioxide. Thereafter, upon hydration of the Earth's crustal rocks, were bonded in carbonates under reactions of:

$$\begin{aligned}&2CaAl_2(Si_2O_8)(\mathit{anorihte}) + 4(H_2O) + 2(CO_2) \rightarrow \\ &\quad Al_4\{Si_4O_{10}\}\{OH\}_8\,(\mathit{kaolin}) + 2Ca\{CO\}_3(\mathit{calcite}) \\ &\quad +110.54 \text{ kcal/mole}\end{aligned} \qquad \text{(Eq. 7.3)}$$

or:

$$\begin{aligned}&4Mg_2(SiO)_4(\mathit{olivine}) + 4(H_2O) + 2(CO_2) \rightarrow \\ &\quad Mg_6\{Si_4O_{10}\}\{OH\}_8(\mathit{serpentine}) + 2Mg(CO_3) \\ &\quad (\mathit{magnesite}) + 72.34 \text{ kcal/mole.}\end{aligned} \qquad \text{(Eq. 7.4)}$$

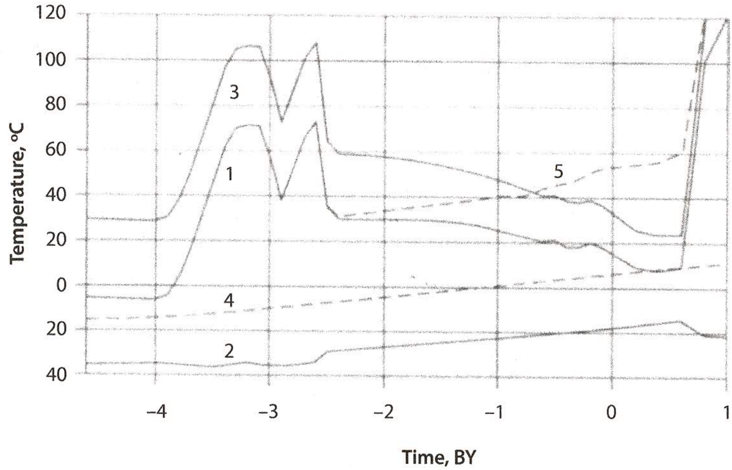

Figure 7.9 Averaged evolution of Earth's climates at a constant Earth's precession angle of $\psi = 24°$. *Curve 1* – Average Earth's surface temperature at sea level estimated using Eq. 2.27. *Curve 2* – Effective Earth's temperature using Eq. 2.25. *Curve 3* – Earth's atmospheric greenhouse effect using Eq. 9.1. *Curve 4* – The absolute black body temperature from Eq. 2.3 at a distance of Earth to the Sun describing the increase, with time, of the Sun's luminosity, *S*. *Curve 5* – Average Earth's temperature assuming that there was no nitrogen consumption by bacteria.

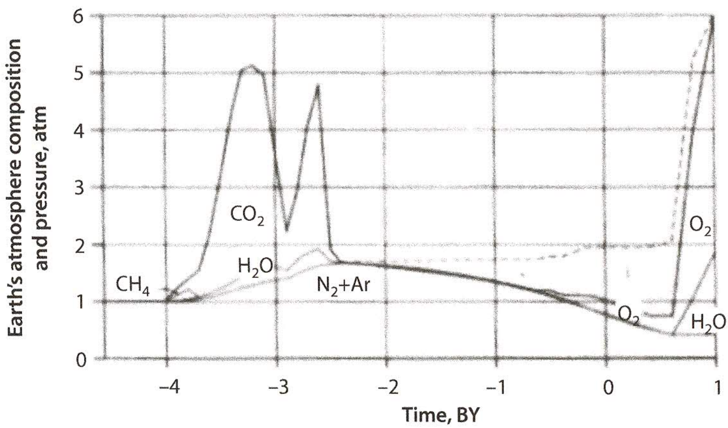

Figure 7.10 Evolution of the Earth's atmospheric composition and pressure evolution with time. The dashed line is the atmospheric pressure in the absence of bacterial consumption of nitrogen.

After reaching a stationary level of oxygen (approximately 230 mbar), nitrogen partial pressure continued to decline, and the atmospheric pressure in Cenozoic began to decline again, resulting in a decline in the atmospheric pressure and a cooling of the climate.

The general decline in atmospheric pressure could not continue without limit, as ≈600 MY in the future, when a drastic increase in the partial pressure of the abiogenic oxygen is anticipated. This problem is the result of Earth's core formation processes shown in Figure 7.9. The suggested increase in near-surface temperature, according to Eq. 2.26, will exceed a temperature of 180 °C resulting in the destruction of all life on the Earth. At this temperature and pressure, there can be no liquid water on the surface of the Earth. The variation of the Earth's atmospheric composition and partial pressures for the life of the planet is shown in Figure 7.10. The only conclusion is that life on Earth is finite and will not continue forever. The time of existence for life on Earth will be ≈4.6 BY, with most of this time (≈4 BY) having already expired with 0.6 BY remaining.