6

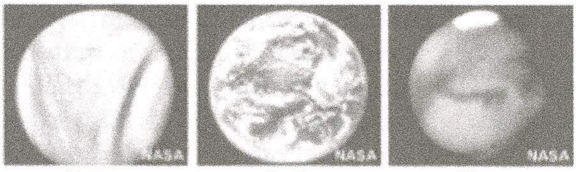
Nitrogen in Earth's Atmosphere

Origin of Earth's Atmospheric Nitrogen

Nitrogen, N_2, is a colorless, odorless and tasteless gas that makes up 78.09% (by volume) of the Earth's atmosphere today. It is nonflammable gas and does not support combustion.

UIGI (2017) notes that the density of nitrogen gas is slightly lower than that of air. It has a low solubility in water and is commonly considered and can be used as an inert gas, although it is not truly inert, as it forms nitric oxide and nitrogen dioxide with oxygen, ammonia, hydrogen, and nitrogen sulfide. The nitrogen compounds are formed naturally through biological activity. Nitrogen compounds are also formed at high and moderate temperature with the aid of catalysts. At elevated temperatures, nitrogen combines with active metals, such as lithium, magnesium and titanium to form nitrides. Nitrogen is required for many biological processes, and used as a fertilizer (often in the form of ammonia or ammonia-based compounds).

Nitrogen condenses at its boiling point, −195.8 °C (−320.4 °F), to a colorless liquid that is lighter than water.



	Venus	Earth	Mars
Carbon Dioxide (CO_2)	96.5%	0.03%	95%
Nitrogen (N_2)	3.5%	78%	2.7%
Oxygen (O_2)	Trace	21%	0.13%
Argon (Ar)	0.007%	0.9%	1.6%
Methane(CH_4)	0	0.002%	0

Figure 6.1 Comparison of composition of Venus, Earth and Mars atmospheres. (After Earth Science, 2014.)

Nitrogen is the most dominant gas in today's Earth atmosphere. Figure 6.1, compares the compositions of the atmospheres of Venus, Earth and Mars. The Earth's atmospheric nitrogen concentration is 78%, as compared to 3.5% for Venus and 2.7% for Mars. Reasons for today's apparent lack of nitrogen in Venus's and Mars's atmospheres are that they appear to have had negligible degassing of their mantles (volcanism or plate tectonics) and absence of bacteria. Two major sources controlling the nitrogen content of Earth's atmosphere have been volcanoes (degassing of mantle) and bacterial-fixing of organic material.

Nitrogen is a moderately active element that reacts weakly with inorganic compounds. There are, however, nitrogen-consuming bacteria, that remove nitrogen gas from the atmosphere and circulate it through soil after being dissolved in water, bonding and fixing it to organic matter. The first and most primitive bacteria, *Procaryotes* and *Archaeans*, probably appeared soon after the emergence of life on Earth. It is likely, that in the Archaean time, the primitive bacteria included some nitrogen-consuming bacteria. Organic matter bonded with nitrogen is found in buried oceanic sediments. Also, nitrogen is bonded in nitrates and nitrites fixed by thunderstorm activity. Thus, bacterial life activity and thunderstorms over a long geological evolution have likely stripped nitrogen from the atmosphere and significantly lowered the partial pressure of nitrogen in the Earth's atmosphere.

Today's nitrogen cycle (Figure 6.2) is a description of how nitrogen is converted into various chemical forms as it circulates among the atmosphere,

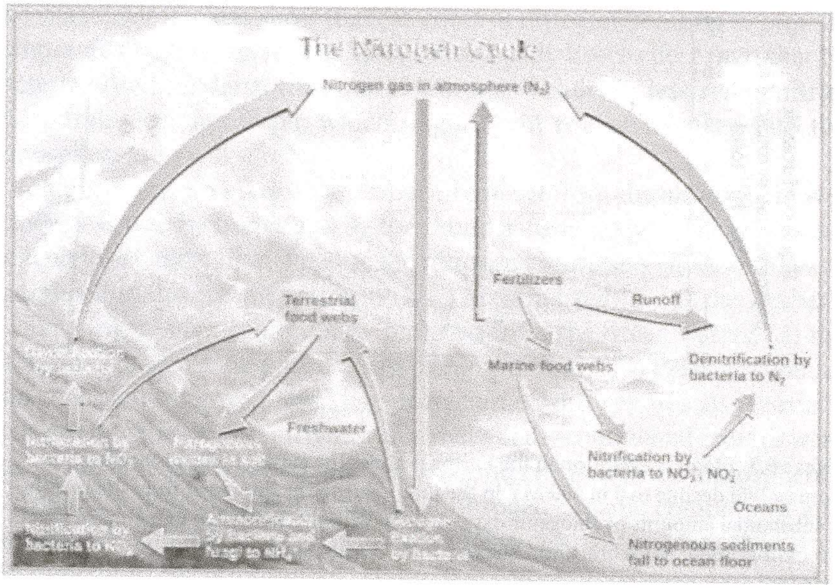


Figure 6.2 Today's nitrogen cycle. (After AP Biology, 2017.)

terrestrial, and marine ecosystems. The bonding of nitrogen is carried in the nitrogen cycle by biological and physical processes (Wikipedia, 2017). Today's cycle of nitrogen is far different from those of earlier time periods, before the development of plants and bacteria. As discussed in this chapter, the Earth's atmospheric pressure, composition and temperature has varied over time, dependent upon the active geological processes.

The nitrogen content in the Earth's atmosphere (Figure 5.1) increased in the Late Archaean time due to introduction of bacteria (biomass) into the oceans (Figures 6.3). This concept is supported by the nitrogen-organic compounds found in the Archaean oceanic sediments. Figure 6.4, *Curve 3*, illustrates the increase in atmospheric partial pressure and atmospheric nitrogen content (see Figure 5.1), as compared to its earlier primordial atmospheric pressure, which was due to degassing from the mantle and loss of other atmospheric volatile gasses by absorption.

During the Proterozoic time, as shown in Figure 5.1, the Earth's atmosphere was almost entirely nitrogen and then the nitrogen content decreased due to an increase in bacterial action which removed nitrogen from the atmosphere. This change in the atmosphere's nitrogen content and lower partial pressure resulted in the cooling of the Earth's surface, which continued through the Proterozoic and Phanerozoic time. Eq. 2.26 demonstrates the relationship between the atmospheric pressure and temperature, the

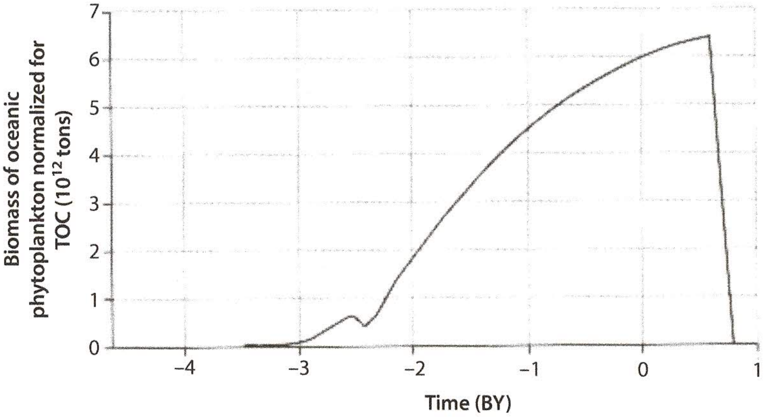


Figure 6.3 Biomass evolution in the Earth's oceans. The authors predict that the biomass will decline to 0 in 600 MY in the future due to the degassing from the mantle in substantial amounts of abiogenic oxygen along with the associated greenhouse effect (Sorokhtin, 1974; Sorokhtin and Ushakov, 2002). (After Sorokhtin *et al.*, 2011, figure 12.7, p. 447.)

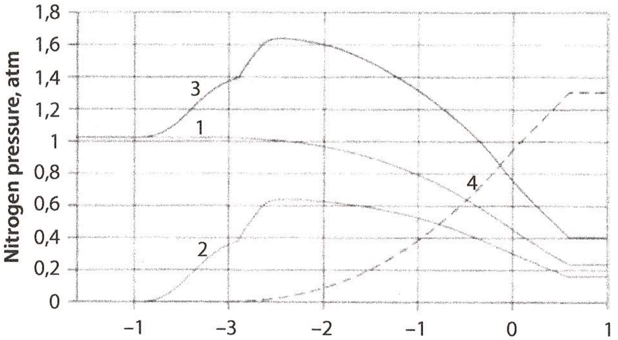


Figure 6.4 Evolution of the Earth's atmospheric nitrogen partial pressure: *Curve 1* – nitrogen of young Earth's primordial atmosphere. *Curve 2* – nitrogen degassed from the mantle. *Curve 3* – pressure of total body of atmospheric nitrogen. Curve 4 – mass of nitrogen removed from atmosphere by nitrogen-consuming bacteria (recalculated using pressure).

Earth's surface temperature declining due to a decline of total atmospheric pressure; decline in the nitrogen's partial pressure is due to a change in nitrogen content of the atmosphere. This total cooling effect on the Earth's surface, over 4.5 BY, has not exceeded 5.4 °C, whereas according to the climatic paradox, the historic cooling over that period reached 70 °C.

This decline in the nitrogen's partial pressure can be attributed to: (1) bacterial metabolism and (2) thunderstorm activity in a humid atmosphere.

The available estimates show that the effect of nitrogen bonding to organic compounds by thunderstorms has a substantially lower effect than that by bacteria. The thunderstorm-bonded nitrogen results in less stable nitrite and nitrate decomposition, which might again release nitrogen into the atmosphere.

On assuming, however, that nitrogen removal from the atmosphere was achieved as well by bacteria as by the thunderstorm activity, the effects are difficult to separate. In calculating the nitrogen absorption effect, one has to consider that the organic nitrogen (N_{org}) accumulated in: (1) the Archean oceanic deposits are continuously removed from the ocean waters, (2) the Archean deposits of the oceanic crust pileup zones, and (3) the plate subduction zones in Proterozoic and Phanerozoic time. Nitrogen was also partially included into the granite-metamorphic rocks of the continental crust or went into the mantle and was partially degassed and released to the atmosphere

The increase of bacterial-bonding of nitrogen-organic compounds and degassing of the mantle in oceanic sediments clearly dominate the nitrogen content of the atmosphere (Figure 6.4, *Curve 3*). Nitrites and nitrates emerging from the thunderstorms are less stable than the nitrogen-organic compounds fixed by bacteria and are likely to be degassed again. Only certain bacteria are capable of consuming and fixing the atmospheric nitrogen to organic matter. These are referred to as nitrogen-assimilating bacteria. Several forms of flora consume nitrogen-organic compounds, e.g., phytoplankton or plants. Flora feed on nitrogen compounds generated by the nitrogen-assimilating bacteria.

Regarding bacterial activity, Wikipedia (2017) presents a partial representation of the nitrogen cycle showing the path of nitrogen: (1) in the atmosphere and (2) soils of the Earth, where a variety of bacterial reactions act on nitrogen gas found in the atmosphere (Figure 6.5).

Estimate of the Earth's Volume of Organic-Nitrogen Sediments

To estimate the volume of bound organic-nitrogen, N_{org}, on the Earth, one can estimate the quantity of organic-nitrogen in the oceanic sediments that has been continuously removed from the oceans through the subduction zones during the Proterozoic and Phanerozoic time. These organic-nitrogen compounds that are partially included are: (1) the granitic-metamorphic rocks of the continental crust or (2) sediments transferred into the mantle. During these processes, nitrogen is partially degassed anew and some re-enters the atmosphere.

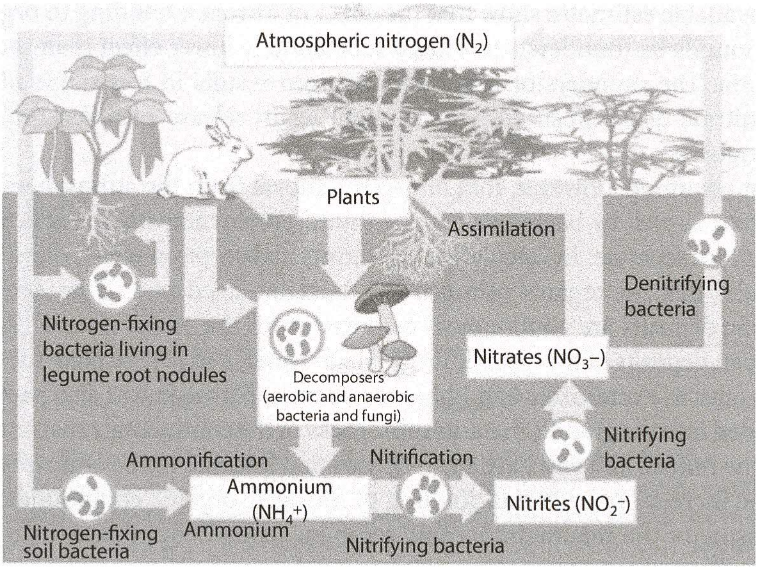


Figure 6.5 Schematic of Nitrogen cycle. (After Wikipedia, 2017), https://upload.wikimedia.org/wikipedia/commons/thumb/f/fe/Nitrogen_Cycle.svg/1200px-Nitrogen_Cycle.svg.png)

According to Ronov and Yaroshevsky (1978) and Ronov (1993), the oceanic deposits (pelagic plus shelf) contain ≈2.7 to 2.86 × 10^{21} g of C_{org} and in the continental deposits ≈8.09 to 9.2 × 10^{21} g of C_{org} are buried. Taking into consideration the effect of avalanche-like deposition of solid terrigenous sediments in the nearshore regions of oceans (Lisitsyn, 1984, 1991) with high organic carbon concentration, a slightly higher value of the present-day mass of oceanic sediments and, correspondingly, of the mass of buried organic carbon, C_{org}, is ≈3.36 × 10^{21} g. The authors estimate that the mass of nitrogen buried in the: (1) sediments of oceanic floor, and its shelf regions is ≈2.35 × 10^{20} g, and (2) continental sediments as ≈5.0 × 10^{20} g. This amount of organic-nitrogen was deposited over the average time of existence for the modern oceanic crust, that is, over the recent 5 MY and on the continents, approximately over 400 MY. To determine the organic-nitrogen (N_{org}) accumulation rate during the past geological epochs, one should consider the fact that the element controlling life evolution in the oceans is phosphorus solubility, of which in the oceanic water is limited (Schopf, 1980). The ocean life has evolved mostly within the photo-active water layer. Still, the phosphorus-saturated deeper water reaches this habitable layer through the upwelling zones. It follows that the oceanic biomass has always been approximately proportional to the mass of the ocean *per se* which is shown in Figure 4.11, *Curve 2*. With this data, it is possible to estimate the biomass of the ocean (Figure 6.3).

If the oceanic biomass is proportional to the mass of oceanic water, then one can account also for the approximate mass of the organic-nitrogen (N_{org}) bonded in the deposits and removed together with them during the Earth's geological history from the oceanic sedimento-sphere into the Earth's mantle through the subduction zones of lithospheric plates,

$$(N_{org})^{\Sigma}_{oc} \approx \frac{N_{org\,oc}}{m^{w}_{oc}} \int_{t=4\times10^{9}}^{0} m^{w} dt, \qquad \text{(Eq. 6.3)}$$

where $(N_{org})^{\Sigma}_{oc}$ is the total organic-nitrogen mass removed from the oceanic reservoir over the time from $t = -4$ BY ago to the present $t = 0$; $(\dot{N}_{org})_{oc} = (N_{org})_{oc}/\tau$ represents the current (N_{org}) burial rate in the oceanic deposits; τ = 120 MY ago is the average age of today's ocean floor; and (m^{w}_{oc}) and $(m^{w}_{oc})_{0} = 1.42\times10^{24}\, g$ are the current value and the present-day water mass in the World Oceans (see Figure 4.11, *Curve 2*).

By numerical integration of Eq. 6.3 shows that during the last 4 BY about 4.3×10^{21}g of nitrogen has been removed from the Earth's atmosphere through marine biota life activity. To this amount must be added the nitrogen preserved in the continental deposits ($N_2 \approx 4.3\times10^{21}$ g of organic nitrogen) over a period of close to 400 MY. Thus, the total nitrogen removed from the atmosphere with the small addition of biogenic nitrogen over the life activity on the Earth is ≈4.82×10^{21}g. This would be equivalent to an atmospheric pressure decline of 945 mbar, which is greater than today's nitrogen partial pressure of 765 mbar.

As shown in Figure 5.1, in the Middle Proterozoic time (2 to 0.8 BY ago), the atmosphere was almost pure nitrogen with traces of radiogenic argon. Earth's temperature was much warmer than today and there were no ice sheets anywhere on the continents (Chumakov, 2004b). Therefore, considering the average elevations of the continents at that time, nowhere did the average annual temperature (even at the poles) drop below 0 °C. The adiabatic theory of the *greenhouse effect* (Figure 2.26) requires that for positive temperatures on the surface of the continents, with the average elevations of 1- to 1.7-km, which were formed in the Middle Proterozoic at the poles, the atmospheric pressure should have exceeded 1.2 atm.

The only way one could explain why the nitrogen partial pressure change of about 0 atm in Katarchaean to 1.4 atm in Proterozoic to today's value of 0.755 is by assuming that along with the mantle-degassed nitrogen there was also an effective mechanism for nitrogen removal from the atmosphere (Sorokhtin, 2005a and b, 2008). It can be explained if the present-day atmosphere contains about 40% of the mantle-degassed nitrogen. The nitrogen partial pressure evolution from the mantle is illustrated in *Curve 2,* Figure 6.4.

Chapter 14 discusses the future general decline of the atmospheric pressure and the increase in the climate severity. The resulting temperature increase will affect the general metabolism of the nitrogen-consuming bacteria resulting in a slowdown in nitrogen removal from Earth's atmosphere and destroying the life present now on Earth. It will establish a new equilibrium state of nitrogen content for the atmosphere. This is anticipated in 660 MY in the future.