HISTORY OF ATMOSPHERIC COMPOSITION

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Contents

Summary

The data on Earth's atmosphere history for the last 4.5 billion years are presented. Between 4.5 and 2.5 billion years (the Archaean and Proterozoic time), the earliest secondary atmosphere contained carbon dioxide (CO_2), methane (CH_4), water vapor (H_2O), carbon monoxide (CO), a little nitrogen (N), and hydrogen (H). Hydrogen in the earliest atmosphere made it weakly deoxidizing. At the end of the Proterozoic time (around 2.5 billion years ago), nitrogen concentration was close to the modern one and changed less as compared to carbon dioxide and oxygen. In Precambrian atmosphere, carbon dioxide was hundreds of times higher than now. With low luminosity of the Sun and high CO_2 content, the ancient atmosphere supported Earth's surface temperature within the limits of maintaining primitive life.

Free oxygen concentration began increasing about 2 billion years ago, and by the end of the Proterozoic, it reached 15-20% of its modern value. In the Phanerozoic time, CO_2 remained rather high, but it rapidly reduced in the second half of the Cenozoic.

The evolution of atmospheric gas composition is closely related to the evolution of the

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biosphere. Atmospheric composition was much affected by life transition from ocean to land in the Devonian period. Warm epochs of the Phanerozoic and Cenozoic time are closely associated with a high CO_2 concentration in the atmosphere, and cooling with CO_2 lowering. In the second half of the Cenozoic, CO_2 started to decrease very rapidly. By the Pleistocene, it was close to its modern value. The empirical data on atmospheric content of greenhouse gases are cited for the last 400 000 years. The current CO_2 and methane growth is associated with their release into the atmosphere due to increased anthropogenic impact.

1. Introduction

Atmosphere (from the Greek words *atmys* meaning steam and *sphaira* meaning ball) is a gaseous shell of the Earth. The mass of the Earth's atmosphere is about 5.15 x 10^{15} tons.

The present atmosphere consists of a mixture of gases. The amounts of these gases in dry atmospheric air and their molecular masses are presented in Table 1.

Gas	**Volume concentration (%)**	**Molecular mass**
Nitrogen	78.08	28.0
Oxygen	20.95	32.0
Argon	0.93	39.3
Carbon dioxide	0.03	44.0

Table 1: Chemical composition of the atmosphere

Dry atmospheric air also contains small amounts of neon, helium, methane, krypton, hydrogen and some other gases. Structure of the atmosphere changes with altitude. Helium predominates above 1000 km, and hydrogen above 5000 km.

The modern atmosphere is of a secondary origin. The Earth's atmosphere has a unique gas composition favorable for developing and flourishing the highest life forms. This gas composition of the atmosphere, optimum for the biosphere, arose as a result of long-term evolution of gases released from the interior part of the Earth due to mantle degassing and to complicated geochemical and biochemical conversions. The proportion of the gases nitrogen, carbon dioxide, and water vapor, composing the modern atmosphere, changed in the course of volcanic activity. Also intrusion processes extracted them from the depth of the planet. The quantitative estimates of atmospheric CO_2 and O_2 in the geological past were calculated from the data on chemical composition of carbonate deposits (see Changes in Biogeochemical Cycles).

Throughout the Phanerozoic (the last 570 million years), atmospheric CO_2 varied within wide range depending mainly on volcanic activity. During individual periods, atmospheric CO_2 was 10 to 15 times above the value that was typical for the pre-industrial epoch (approximately before 1850). At the present time, due to the burning of fossil fuel (gas, oil, coal, and other kinds of carbon fuel) a part of carbon dioxide,

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methane and other gases buried in the Earth's crust in the course of geological history are returned back into the atmosphere.

A close relation has been established between the stages of evolution of organisms and variations in the chemical composition of the Earth's atmosphere. The data on variations in concentration of carbon dioxide throughout geological history can be used to study the present anthropogenic climate change caused by the growth of atmospheric CO_2 due to the burning of coal, oil and other kinds of carbon fuel.

2. Evolution of the Ancient Atmosphere

The Earth, as all the inner planets, is characterized by small amount of volatile substances. The mass of the hydrosphere comprises as much as 0.024% and the mass of the atmosphere - 0.00009% of the Earth's total mass. This very small amount of volatile substances is connected with the formation of our planet in that part of the primary nebula where the amount of volatile substances was insignificant (see History of Planetary and Geological Factors).

The evolution and composition of the Earth's atmosphere are directly related to the evolution of the Sun. The Sun is a rather typical star, which is attended by a family of smaller bodies. The Earth is located at such a distance from the Sun that the temperature of its surface during different periods changed, but within a small range. If the luminosity of the Sun had been 1.5 to 2 times greater, the Earth would have been like Venus with a dense carbon dioxide and steam atmosphere. With lower luminosity of the Sun, the Earth could have frozen like Mars (see Earth System: History and Natural Variability).

Thus, the evolution of the atmosphere depended on the evolution of two external factors: the evolution of the Sun and the evolution of the Earth itself. The main factors were a gradual damping of upper mantle degassing accompanied by the Sun's increasing luminosity. In practice, these two processes compensated for each other. This allowed the Earth's climate to remain almost steady throughout billions of years during a time interval favorable for developing an organic life.

During the evolution, the Earth's atmosphere endured considerable changes due to different factors: dissipation of atmospheric gases into space, disintegration of molecules by solar radiation, chemical reactions between atmospheric gases and rocks, and accretion (catch) of space matter (e.g. meteorite matter).

The evolution of the atmosphere may be divided into three stages. The first stage includes the Archaean and Early Proterozoic time, when the earliest (ancient) oxygen-free atmosphere formed. The second stage covers the greater part of the Precambrian time to the beginning of the Phanerozoic. At this stage, free oxygen appeared due to life activity of blue-green algae. The third stage, covered with a bulk of data, including the quantitative ones, is the Phanerozoic era (the last 570-600 million years).

2.1 The Earlier Secondary Earth's Atmosphere (the Precambrian and Cambrian Period)

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Supposedly, the earlier secondary atmosphere began forming as long ago as 4 billion years. The gas composition of that atmosphere differed greatly from the modern one and consisted mostly of the gases accumulating to the atmosphere from the degassing of upper mantle. Carbon monoxide (CO), carbon dioxide (CO_2), water vapor (H_2O), methane (CH_4), a small amount of nitrogen (N), and hydrogen (H) predominated in the gas composition of that atmosphere. Free oxygen (O_2) could not have been present; even modern volcanic gases contain no oxygen.

The amount of hydrogen in the Earth's atmosphere depended on the balance between its income to the atmosphere with elevated volcanic activity, and its loss to space. Due to hydrogen, the ancient atmosphere was weakly deoxidizing. Carbon dioxide in Precambrian atmosphere was probably ten times greater than its modern mass. Since that time its mass has been gradually reducing. This major trend had numerous accompanying maxima and minima associated with increased or decreased volcanic activity (see Global Climatic Catastrophe (Volcanism and Impact Events).

Two billion years ago, the Earth's atmosphere consisted of water vapor, carbon dioxide, methane, and ammonium, with little or no free oxygen. Supposedly, the high content of greenhouse gases in the ancient Earth's atmosphere, primarily. carbon dioxide, methane, and water vapor, prevented heat radiation loss into space. This provided rather high surface temperature with a comparatively low Sun's luminosity in the Archaean and the Proterozoic time. About four billion years ago the Sun's luminosity is believed to have been 28% lower than at present. Over the last four billion years the Sun's luminosity has been gradually increasing, and carbon dioxide mass had been decreasing due to the reductions in the rate of degassing of the Earth's upper mantle. These two contradictory processes had been preserving a steady Earth's climate for many millions of years.

During the Archaean time free oxygen was not above 0.1% of its modern value. Since then the amount of free oxygen has increased by two mechanisms: 1) due to water molecule photodissociation, and 2) as plantlike primitive organisms called blue-green algae evolved and multiplied, they added oxygen to the atmosphere, around 2.5 billion years ago. Stromatolites provide evidence for dating the first life forms on earth. A stromatolite is a laminated or conical sedimentary rock structure formed about 3.5 billion (3 500 000 000) years ago, primarily, in Precambrian shallow pools. Such primitive organisms caused carbon dioxide (CO_2) and water to produce via photosynthesis carbohydrates, and as a result free oxygen was released.

However, up to 1.8 billion years ago oxygen mass had been less than 1% of its modern value. By the Cambrian boundary, it was already several percent of its present value. Layers with strongly oxidized iron compounds aged at 1.8 to 2.0 billion years indicate a sufficient amount of free oxygen in the atmosphere. Figure 1 presents the oxygen mass changes in the Upper Proterozoic and the Phanerozoic.

As seen from Figure 1, from 2.0 billion years ago till the beginning of the Phanerozoic time oxygen increased in the atmosphere with an average rate varying comparatively little.

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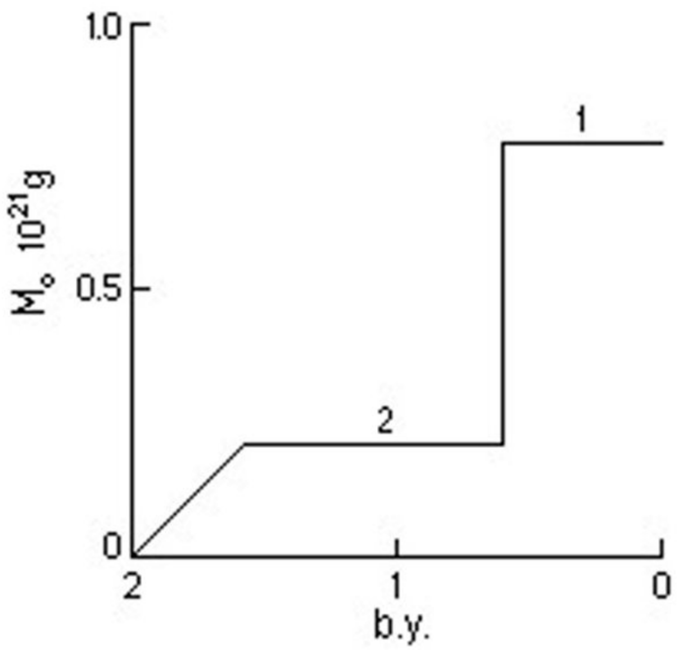

Figure 1: Changes in oxygen mass, Mo: 1 - Phanerozoic, 2 - Late Proterozoic
(From: M. Budyko, A. Ronov, and A. Yanshin "History of the Earth's atmosphere", Springer Verlag, 1987)

Carbon dioxide was another very important component of the ancient atmosphere. Its concentration decreased rapidly between four and two billion years ago, because of changes in the rate of upper mantle degassing. Changes in atmospheric CO_2 for the last billion years are shown schematically in Figure 2.

It is suggested that in the early Precambrian time, atmospheric carbon dioxide cycle was analogous to the modern one with CO_2 mass 100 or more times exceeding the modern. The high CO_2 concentration in the atmosphere supported a rather high surface temperature during the Precambrian with a relatively low, as compared to the present, Sun's luminosity. Without this assumption, it is very difficult to explain the fact of continuous existence of living organisms in the Precambrian.

Throughout the entire Precambrian, there was a general trend towards decreasing CO_2. At the same time, rhythmic oscillations of CO_2 mass occurred depending on the rate of upper mantle degassing.

Along with changing CO_2, O_2 and other gases in the Precambrian atmosphere, there were variations in nitrogen (N). Throughout the greater part of the Earth's history, the amount of nitrogen is assumed to change less than the variations in CO_2 and oxygen. Nitrogen, like carbon dioxide, was released into the atmosphere by degassing. Assuming that the secondary atmosphere began to form around four billion years ago, we may evaluate that about 3.5 billion years ago the amount of nitrogen in the Earth's atmosphere was half its modern mass, and about two billion years ago already about 95%. The cycle of atmospheric nitrogen exchange with the lithosphere is long and lasted about two billion years. Nitrogen-fixing bacteria in soil and natural waters extracted nitrogen from the atmosphere. Therefore, ammonium and other nitrogen compounds formed.

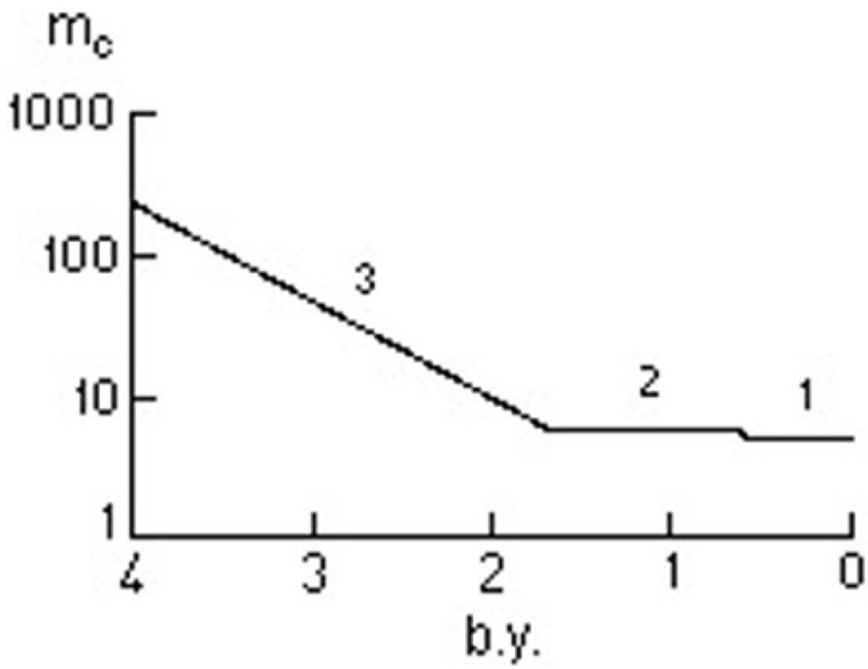

Figure 2: Changes in relative mass (m_c) of carbon dioxide (CO_2): notation "b.y." means billions years ago. *(From: M. Budyko, A. Ronov, and A. Yanshin "History of the Earth's atmosphere", Springer Verlag, 1987)*

So, by the end of the Proterozoic carbon dioxide in the Earth's atmosphere was several times above the modern level, and oxygen concentration was from 15 to 20% of the present value. The amount of nitrogen differentiated little from the modern.

3. Atmosphere Composition during the Phanerozoic Time

Today there are many studies dealing with the development of a quantitative model of changes in Phanerozoic atmosphere composition (for the last 600 million years). The empirical information about the atmospheric composition during this time is based on geological and geochemical data from sedimentary and volcanic rocks. These data were the basis for building a quantitative model of atmosphere gas composition for the Phanerozoic time. There are some other methods for assessing atmosphere gas composition for the same period. In particular, some studies deal with the relationships between carbonate formation and CO_2 concentration in the atmosphere. The idea of the American geochemist R. Berner consists in assessing the rate of CO_2 income to the atmosphere by the data on sea floor spreading.

Figure 3 presents the data on changing oxygen and carbon dioxide during the Phanerozoic. An elevated oxygen amount during the Cambrian promoted a wide distribution of skeleton forms of marine animals. In the mid-and late Ordovician another oxygen maximum occurred and promoted the formation of early fishlike vertebrates.

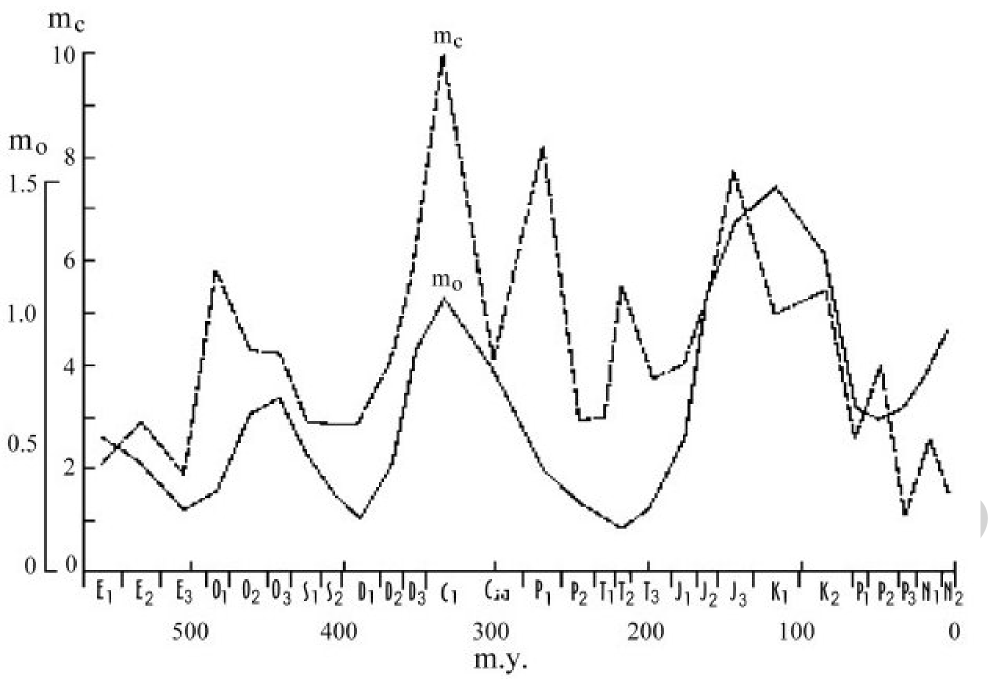

Figure 3: Change in relative mass of carbon dioxide (m_c) and oxygen (m_o) during the Phanerozoic *(From: M. Budyko, A. Ronov, and A. Yanshin "History of the Earth's atmosphere", Springer Verlag, 1987)*

Although there was a general trend of increasing oxygen in the Phanerozoic, its main period of growth was during two geological periods: over the Devonian to early Carboniferous and during the late Triassic to Jurassic. At that time, first birds and mammals appeared. It is believed that at the Early to Late Cretaceous boundary (about 100 million years ago), there was a drastic oxygen content reduction. Its content dropped from the values of one and half times higher than the modern ones, in the Triassic, the Jurassic, and the Early Cretaceous time, to the values close to the modern ones. Quite recently, these calculations have been confirmed by empirical data on the atmosphere composition during the Mesozoic obtained from air bubbles retained in fossil amber.

By correlating the data on atmospheric oxygen with living matter development, one can assume that during the epochs with elevated oxygen concentrations the conditions were more favorable for increasing the diversity of living forms and the appearance of forms with a comparatively high metabolism—forms whose existence at lower oxygen levels would have been impossible. Thus, reduced oxygen during the Late Permian and Triassic time retarded the formation of mammals for about one hundred million years. This class of vertebrates spread only with O_2 concentration growth in the second half of the Triassic.

The living nature effects of carbon dioxide concentration variations occurred along with the influence of oxygen. Variations in CO_2 content in the Phanerozoic primarily changed photosynthetic productivity. In the history of Phanerozoic atmosphere, an event of great importance was the movement of life (as land vegetation) to land in the Devonian time**.** This event led to an 800-fold increase in the Earth's biomass. This change had to exert a pronounced effect on the course of geochemical processes in the Earth's biosphere and cause certain modifications in atmosphere composition. With an average CO_2 concentration for the entire Phanerozoic of 0.10 to 0.15%, there are at least six maxima in CO_2 concentration exceeding this average value. In this case, during the Phanerozoic an average CO_2 concentration turned out to be very close to its optimum to start photosynthesis.

Carbon dioxide maxima are recorded in the Early Ordovician, and in the Devonian and Early Carboniferous. In the Carboniferous, atmospheric CO_2 concentration reached its maximum for the entire Phanerozoic. The third maximum occurred in the Early Permian, the fourth in the Middle Triassic, the fifth in the Late Jurassic, and the sixth in the Late Cretaceous. The fifth and sixth maxima represent a portion of a prolonged period with high CO_2 concentration embracing the greater part of the Jurassic and almost the entire Cretaceous.

The Cretaceous period occupies a specific position in the Earth's history. It had several large biogenetic events: "Planktonic explosion" and mass extinction at the Senoman-Turonian boundary (about 92 Ma) and Maestrichtian, at the end of the Maestrichtian time, at the Cretaceous/Cenozoic boundary, about 65 Ma.

In the second half of the Cretaceous, there was a trend toward atmospheric CO_2 reduction. In the Maestrichtian, CO_2 concentration was the lowest during the entire Phanerozoic. A rapid concentration reduction (almost by half) occurred between 72 and 65 million years ago, and at the end of the Maestrihtian time CO_2 concentration started again to grow, probably, due to intensification of volcanic activity **(**see Global Climatic Catastrophe (Volcanism and Impact Events).

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