Proterozoic slushball Earth and generation of excess oxygen unachieved by photosynthesis

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Abstract

According to the Earth-scale top model, the Earth's axis was tilted approximately 1.8 billion years between 2.7 billion to 900 million years ago. This resulted in the freezing of the equatorial zone and the recognition of a Slushball Earth, explaining the Pongola, Huronian, Sturtian, Marinoan, and Gondwana - glaciations as well as numerous other historical events of the Earth. The hypothesis that nitrogen, oxygen, and water were formed due to nuclear transmutation at high temperatures and pressures, suggests that excess oxygen was produced during photosynthesis and nitrogen and water were expelled into the atmosphere from magma reservoirs in the upper mantle through an open system which caused volcanoes in ocean islands. The evolution of atmospheric oxygen concentration leading to the development of life over the past 400 million years, can be explained by the nitrogen released into the stratosphere through open systems while the magma reservoirs are blocked.

1. Introduction

Since Earth's formation, it has experienced several periods of cold weather, known as glacial period or glaciation. The oldest known ice age is the Pongola, which occurred in South Africa approximately 2.9 billion years ago, while the most recent is the Late Cenozoic ice age, which continues to this day[1]. Following W. B. Harland's theories regarding Neoproterozoic glaciers[2], the "Snowball Earth" hypothesis was first proposed by J. Kirshvink[3] in 1992. Then, P. F. Hoffman[4] summarized the results of a cap carbonate survey in Namibia, South Africa, in the so-called "global freezing" hypothesis. The Snowball Earth hypothesis asserts that the entire Earth was completely covered in ice sheets and sea ice, including near the equator, in the last stage of the early Proterozoic Huronian Ice Age (2.45—2.2 billion years ago) and the Late Proterozoic Sturtian and Marinoan Ice Ages (730—635 million years ago). Proponents of this theory have challenged the geological evidence for global glaciation and the geophysical feasibility of ice- and mud-covered oceans[5,6] and have emphasized the difficulty of escaping a total freeze. Many questions remain with regards to this hypothesis, including whether the Earth was either a perfect snowball or a "slushball" with a thin equatorial open water zone (or seasonally open water zone)[7]. A competing hypothesis to explain the presence of ice on the equatorial continents is based around the Earth's axial tilt angle being approximately 90°. Williams reported a high-obliquity low-latitude ice and strong seasonality (HOLIST) hypothesis based on a large inclination in the Earth's axis[8]. However, his hypothesis has been refuted because of its mechanical difficulty[3] and scarce supporting evidence[4].

Hara[9] proposed another explanation for the phenomenon of low-latitude glaciation based on Earth-scale top model, that is, an extended period of time in a sideways inclination over 1.8 billion years from about 0.9 to 2.7 billion years at an axis of rotation tilt angle $\theta \sim 90°$, which would result in weak sunlight over the equatorial zone, resulting in a long-running susceptibility to freezing. This alternative to the Snowball Earth hypothesis is the so-called "Slushball Earth" hypothesis.

Ice entombed events are believed to have caused the mass extinction of protists, known as the Great Extinction, and the subsequent leap in biological evolution, known as the Cambrian Explosion. The emergence of oxygen-breathing organisms and multicellular organisms, known as the Ediacaran biota are thought to be closely related to ice-entombed events. Our interests lie in the Slushball Earth hypothesis and the generation of excess oxygen during glacial periods, from 2.7 billion years ago to present. Due to the unavailability of directly observed astrophysical and geophysical data to explain the variations in the axial tilt of the Earth system model and the formation of oxygen, respectively, these questions need to be analyzed using circumstantial evidence and insights gained into Earth's historical events using other types of data.

2. Neoproterozoic Slushball Earth

The evolution of the tilt angle of the Earth has greatly influenced its dynamic, climatic, and biotic development. Williams first proposed this possibility based on the normal climatic zonation during the Phanerozoic, the paradoxical Late Proterozoic glacial climate, the seeming reserve climatic zonation of the Precambrian in general, and the single giant impact hypothesis for the origin of the Moon[10]. Because he did not show the precise variation of Earth's obliquity over its history, the variation in the obliquity was thought to be impossible,

Hara[9] proposed another explanation for the phenomenon of low-latitude glaciation based on Earth-scale top model, that is, an extended period of time in a sideways inclination over 1.8 billion years. This model simulated the change in the inclination of the spin axis of Earth after starting at $\theta = 179.5^\circ$ provided that actual real-Earth values $(C\text{-}A)/C = 0.0034$ and $\omega = 366.25\ \Omega$ (365.25 spins about its axis a year and one geometric spin generated by one revolution around the Sun[11]), based on the well-known precession-nutation theory with the hypothetical gyroscope-effect, where θ is the direction of an axial tilt angle from the north ecliptic pole, C and A are moments of inertia along and transverse to the axis of symmetry, respectively; ω and Ω are spin and revolution rates, respectively (Supplementary Information S1[hereafter, referred to as (SI)]). Figure 1 shows the reversing motion of the symmetry axis of the Earth-scale top from 4.6 billion years ago to the present time, along with various geophysical and biological events in Earth's history. This curve is distinct over a long time-interval (1.8 billion years) of sideways tilt ($\theta \approx 90^\circ$) from 2.7 to 0.9 billion years ago, corresponding to low-latitude glaciation.

From the results of a cap carbonate survey in Namibia, P. F. Hoffman[4] reported that the "global freezing" hypothesis explains many extraordinary observations in the geologic record of the Neoproterozoic world: (1) the presence of striated iron deposits; (2) evidence of long-lived glaciers at sea level in the tropics; (3) mystery of the presence of cap carbonate rocks; (4) Carbon isotope changes associated with glacial deposits. Since Hoffman refuted Dr. Jenkins' and Dr. Skotese's thesis[12] with four striking features of late Proterozoic glacial deposits, here, we will attempt to answer four questions, taking the Proterozoic Slushball Earth hypothesis into consideration:

(i) Presence of striated iron deposits:

Striped iron ores are alternating accumulations of iron oxide-rich and silica-rich layers, and are widely distributed throughout the world, including special Austria and Brazil. This deposit is known to have formed in large quantities approximately 2.5 to 2 billion years ago[13,14]. This indicates that the ice-covered oceans were anoxic because gas exchange with the atmosphere was blocked, and divalent iron ions were dissolved under anoxic conditions. Since continental formation began in the early Proterozoic, and by the late Proterozoic the Rodinia supercontinent assembled near the equator[15], the formation of striated iron ores can be explained by the freezing of equatorial regions associated with Earth's tilting (Fig. 1). However, the fact that few striated iron ores have formed since their formation approximately 1.8 billion years ago implies that the oxygen concentration in the atmosphere has increased to some extent, as illustrated in Fig. 2. On the other hand, the striated iron ore deposits in the Late Proterozoic, which have not formed in a billion years, are thought to have formed again because magmatic activity caused the supply of reducing materials from the submarine hydrothermal system, resulting in a hypoxic environment[3].

(ii) Paleomagnetic evidence of the existence of continental ice sheets in equatorial regions:

When sedimentary rocks form, the magnetic minerals within them tend to coincide with the Earth’s magnetic field. As a result, paleomagnetism can be used to estimate the latitude at which the rocks were deposited. The paleomagnetic position of glacier-derived deposits (e.g., dropstones) suggests that glaciers extended from land to sea level at tropical latitudes at the time that they were deposited[16]. Currently, the only sediments known to have been deposited at low latitudes are the Elatina sediments of Australia, whose depositional age is well constrained and the signal is clearly original[17]. Based on the magnetic orientation of tiny mineral grains in glacial sediments, Harland asserted that all continents had assembled near the equator in the Neoproterozoic[2]. The long-lived sideways tilt ($\theta \approx 90°$) for 1.7 billion years in Fig. 1 explains how glaciers could have survived tropical heat.

(iii) Existence of cap carbonates in Neoproterozoic glacial times:

Neoproterozoic glacial deposits are blanketed almost everywhere by carbonate rocks[4]. The existence of cap carbonates indicates that carbonates were abruptly formed in warm, shallow seas due to sudden climate change after the glaciers dropped their last loads. This is because a decrease in the axis of rotation inevitably raises temperatures and melts glaciers in equatorial regions. The thick sequences of carbonate rock are the expected consequence of global warming unique to the transient aftermath of the Slushball Earth, corresponding to recovery from a 90° tilt of the axis of rotation starting at approximately 900 million years.

(iv) Carbon isotopic variations

Carbon isotope ratios ($^{13}C/^{12}C$) show anomalously large values (~ 10‰) below the glacial deposits, but which begin to decline just before the glacial deposits, dropping to values of -6‰ in the immediate vicinity of the glacial deposits[3]. This value is that of volcanic gases supplied to the atmosphere and ocean. This negative anomaly in carbon isotope ratios suggests an almost complete cessation of photosynthetic activity by organisms shortly after the glacial period, (*i.e.*, the Great Extinction of life 0.44 billion years ago (late Ordovician period) and 0.36 billion years ago (late Devonian)[18], corresponding to 74.2° and 67.5°, respectively).

However, there are several problems with designating a glacial origin for cap carbonate[19]: (1) dissolution of carbonates owing to ocean acidity when carbon dioxide concentrations are high; (2) The uncertain existence of cap carbonate.

Considering the Slushball Earth hypothesis, a number of mechanisms have been reported for the onset of frozen Earth, including supervolcano eruptions, reduced atmospheric concentrations of greenhouse gases, such as methane and carbon dioxide and changes in solar energy output. Regardless of the trigger, the initial cooling may have eventually frozen the equator as cold as modern Antarctica owing to the reflection of solar energy back into space (increased Earth albedo) caused by the increased surface area of the Earth covered in ice and snow. Furthermore, the positive feedback would have cooled the Earth further.

Although the existence of glaciers is not disputed, the idea that the entire planet was covered in ice is disputed. Some scientists therefore postulate the “Slushball Earth”, in where sediments are only formed in open water or under rapidly moving ice, or where the hydrological cycle continued in thin ice-covered waters[7]. Computer modelling using energy balance and general circulation models suggests that large areas of the ocean should have remained ice-free and argues that “hard” snowballs are not plausible[20].

A theory that neatly explains the Slushball Earth hypothesis is the overturning of the Earth’s axis hypothesis, as proposed by Hara, which spans a period of 1.8 billion years elapsed from about 2.7 to 0.9 billion years ago. As shown in Fig. 1, the emergence of anaerobic cyanobacteria, Pongola glaciation, generation of oxygen in the oceans, generation of plants, and generation of atmospheric oxygen occurred before the 90° axis rotation of Earth; whereas, the onset of continental development, Hugo-Anglian glaciation, formation of the solid inner core, formation of continents in the equatorial region, and the development of continents after the formation of the Gondwana supercontinent occurred during the 90° tilt. The Earth’s axial tilt began to gradually decrease, accompanied by the Sturtian and Marinoan glacial periods. With the evolution of the Pangaea supercontinent, the Gondwana ice age arrived, leading to the present day axial ratio of 23.5°.

The glaciers began to recede around 900 million years ago due to a decrease in the tilt of the Earth’s axis and a higher concentration of carbon dioxide in volcanic gases and methane gas in the atmosphere due to global warming, followed by a further decrease in temperature due to the weathering of rocks and re-dissolution of carbon dioxide and methane gases into the ocean, resulting in the Sturchian glaciation, followed by the Marinoan and Gaskiers glaciations. However, as the major glacial episodes ended millions of years before the Cambrian explosion, there were three or four smaller glacial periods during the Late Neogene because of these icehouse–greenhouse cycles. When ice melted on Slushball Earth, freshwater layers on land and ocean surfaces provided many new opportunities for biological evolution.

3. Generation Of Excess Oxygen Unachieved By Photosynthesis

Oxygen gas plays a major role in driving evolution, associated with both the dramatic development of life and mass extinctions. Here, we note the generation of excess oxygen unachieved by photosynthetic reactions on Slushball Earth. Change in O_2 concentrations can be divided into three time periods[21,22] (http://www.windows2universe.org/earth/past/oxygen_buildup.html)[23]: very low content before 2 billion years, rapid accumulation (popularly known as “Great Oxidation Event”(GOE)[22]) in the Precambrian era from 2 to 0.42 billion years ago, and saturation content from 0.42 billion years ago to the present time. The results are summarized in Fig. 2. We can find three-time period (3.0, 1.9 and 0.8 billion years ago) enhancements for the great oxidation event. The formation of a small amount of free O_2 on the sea surface by ultraviolet photochemical reactions[24] in the Archean era can be expressed as:

$2H_2O + 4hv \rightarrow 4e^- + 4H^+ + O_2$ (1)

Fig. 2 Changes in concentration of atmospheric O_2 from 4.5 billion years ago to the present time, using data obtained by three reserachers[21–23]. The inset shows a logarithmic plot of partial pressure of O_2 gas against time since 4.5 billion years ago. Four representative glacial periods correspond to rapid increases in partial pressure of oxygen gas.

According to the present consensus[25], oxygen gas was generated as a result of photosynthetic activity. After the first oxygenic photosynthesis by anaerobic cyanobacteria from 3.5 billion years onward, aerobic photosynthesis by plants, algae, and cyanobacteria (eubacteria) produced oxygen gas and carbohydrates from H_2O and CO_2 since 2.7 billion years ago. Photosynthetic reactions can be represented by a single well-recognized formula given by equation (2)[26]:

$6CO_2 + 6H_2O + \text{light energy (2,870 kJ/mol)} \rightarrow C_6H_{12}O_6 \text{ (glucose)} + 6O_2$. (2)

It is known that 1 mol of CO_2 produces 1 mol of O_2 from Eq. (2). In other words, the volume of the reaction did not vary. Therefore, the rapid increase in oxygen gas since 2 billion years ago cannot be explained solely by photosynthesis because the absolute amount of carbon dioxide is too small[27].

Fukuhara proposed a model for the formation of nitrogen, oxygen, and water using circumstantial evidence based on the history of Earth’s atmosphere[27,28]. This hypothesis suggests that endothermic nuclear transformation changes the carbon and oxygen nuclei confined in the aragonite ($CaCO_3$) lattice in magma reservoirs into nitrogen and helium nuclei. Nuclear transformation is enhanced by the attraction caused by high temperatures (≥ 2510 K) and pressures (≥ 58 GPa) in the upper mantle. We obtained Eq. (3) for the completely closed system by the subsequent reactions with photons (γ) and neutrons (n), as shown in SI S2:

$2\,^{12}C + 2\,^{16}O + 4e^* + 4\bar{\nu}_e + 2\gamma \rightarrow {}^{14}N_2\uparrow + 1/2\,^{16}O_2\uparrow + {}^{1}H_2{}^{16}O\uparrow + 2n - 10.58\text{ MeV}$ (3)

Fig. 3 Schematic illustration of nuclei transformations in a magma reservoir of an ocean island and a middle ocean ridge. N_2, O_2, and H_2O are produced in the magma reservoir in the upper mantle, and ^{3}He and ^{4}He are formed from reservoirs of the lower mantle.

When we focus on igneous gases in magma reservoirs in the upper mantle, we see that the nuclear transformation is under open systems with lids, such as magma materials released into the atmosphere, holding high temperatures and pressures (Fig. 3), because of a depth of over 600 km. Here we define the mean blockade of craters as $0 \leqq \bar{x} \leqq 1$, as follows:

$\bar{x} = \sum_{i=1}^{n} x_i\left(T\right)/n$, (4)

where $x_i\left(T\right)$ is the blockade degree exhibited by the *i*-th ocean-island-type volcano during a certain period *T*. Strictly speaking, the right-hand term of Eq. (1) in SI 2 is first separated into two parts, $(1-\bar{x})(2^{14}N + {}^{4}He)$ and $\bar{x}\,(2^{14}N + {}^{4}He)$, when $\bar{x} \neq 1$, and the successive nuclear reactions shown in SI S2, equations (2)−(5) are only applied to the latter. Thus, we obtain:

$4^{12}C+4^{16}O+8e^{*}+8\bar{\nu}_e+ 4\bar{x}\gamma \rightarrow 4(1-\bar{x})^{14}N_2\uparrow+4(1-\bar{x})^{4}He\uparrow+2\bar{x}^{14}N_2\uparrow+\bar{x}^{16}O_2\uparrow+ 2\bar{x}^{1}H_2^{16}O\uparrow+4\bar{x}n$ (5)

As water vapor circulates in the atmosphere to form rain and He gas is easily released from the troposphere into the stratosphere, we only consider atmospheric nitrogen and oxygen.

The following equation is obtained as the concentration of oxygen gas X from the right-hand term in Eq. (5) ($O_2/N_2 = \bar{x}/2(2-\bar{x})$), therefore:

$X = \bar{x} / (4- \delta -\bar{x})$, (6)

where δ is the nitrogen released into the stratosphere when the magma reservoirs are blocked. The causes of the blockade are considered to be the sealing of craters by tenacious lava and thick frozen snow (or ice). Figure 3 provides a schematic illustration of the formation of $2\bar{x}$ mol nitrogen and $\bar{x}$ mol oxygen in the magma reservoir of the upper mantle and $4(1-\bar{x})$mol nitrogen in the atmosphere by an open system with a mean blockade $\bar{x}$. While, ^{3}He and ^{4}He are produced by two- and three-body nuclear fusions, respectively, of deuterons confirmed in hexagonal FeDx core-centre crystals, since they are released from mid-ocean ridge islands derived from the proto-plume such as Baffin and West Greenland Islands[29,30] through the lower mantle[31]. In this study, we only considered nitrogen and oxygen interacting with the troposphere. We calculated the oxygen concentrations using Ward's atmospheric oxygen concentrations over the last 400 million years[32]. The results of which are shown in Fig. 4. The maximum oxygen concentration did not exceed 30% over 400 million years to date. In the inset of Fig. 4, the curves of oxygen concentration versus mean blockade are shown as functions when the values of δ are 0, 1, 1.5, 2, 2.6, 2.7 and 2.8 [equation (6)] over 400 million years. Surprisingly, the oxygen concentrations over

400 million years (Ward's data) was approximately expressed as a function of the mean blockade when δ was 2.7. This indicates that the amount of nitrogen gas released into the stratosphere has been constant over 400 million years and the percentages of the release, $100\delta/$ (4 – $2\bar{x}$), are 76 ± 3% using the relation that $\bar{x}$=0.14 – 0.30 for X = 12 – 30% which are obtained from a curve corresponding to δ =2.7 (Fig. 4, inset). These results indicate that the reaction in the volcano was open. The fact that the present oxygen concentration of 20.8% corresponds to the mean blockade of magma reservoirs, $\bar{x}$= 0.27 (Fig. 4, inset), is very suggestive in view of volcanic activity. Basalt is less viscous but tends to cap volcanoes, as well as freeze. This is reasonable because the lid of the craters must be opened periodically.

Fig. 4 Relationship between atmospheric oxygen concentration, X, and nitrogen gas portion δ released into the stratosphere over the last 400 million years, which are obtained using a computational technique. Inset: Relationship between oxygen concentration, X, and the mean blockade of magma reservoirs, $\bar{x}$, when δ=0, 1, 2, and 2.7. Four red closed circle are obtained from equation (7) at the values of δ=3 and α=0.27.

The above results are those when only the nitrogen gas release was considered and we introduce briefly a trial that the oxygen gas release is simultaneously considered.

A model that the loss of oxygen is proportional to α times the molar volume ratio of oxygen to nitrogen gases is shown in Eq. (7):

$$X = \frac{\bar{x} - \alpha\left(\frac{\bar{x}}{4-2\bar{x}}\right)\delta}{4-\delta-\bar{x}+\alpha\left(\frac{\bar{x}}{4-2\bar{x}}\right)\delta}$$

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We tried plots of X vs. $\bar{x}$ changing in the values of δ and α, and obtained a curve which coincides with the curve of δ = 2.7 in the inset of Fig. 4 only at the values of δ = 3.0 and α = 0.27. Four points are indicated by red closed circles in the inset. It is known that the percentages of the oxygen gas release, 100α ($\frac{\delta}{4-2\bar{x}}$), are 23 ± 1% and those of the nitrogen gas release, 100δ/(4 – $2\bar{x}$), are 84 ± 4% using the relation that $\bar{x}$= 0.14-0.30 for X = 12-30%, namely the loss of oxygen is about one fourth of the loss of nitrogen.

4. Conclusions

In this study, we present a "Slushball Earth" model to explain the occurrence of glaciation and several other geohistorical events. The fact that the evolution of oxygen concentrations up to 400 million years ago, expressed in terms of the mean blockade of ocean-island-type volcanos, $\bar{x}$, and the nitrogen released into the stratosphere while the reservoir was blocked, δ, enhanced the responsibility for the generation of excess oxygen by open system reactions with the blockade of craters at a certain frequency. Ward’s data analysis highlighted two important values, $\delta = 2.7$ and $\bar{x} = 0.22 \pm 0.08$ for 12 – 30% oxygen concentrations over 400 million years. A trial model that both the release of nitrogen and oxygen gasses were considered led to the result that δ is not 2.7 but 3.0, and α which represents a release ratio of oxygen to nitrogen is 0.27, that is, the loss of oxygen gas is about one fourth of the loss of nitrogen gas. We excluded H_2O from the atmospheric composition in this study because its form is liquid or solid, but its mass is nearly equal to $\bar{x}O_2$ in Eq. (5). Thus, nuclear transformation is also a strong candidate for the origin of water on Earth.

Declarations

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Author Contributions

M.F. wrote the paper and supervised all of the work. S. T. devised and calculated the open system reactions model with the blockade of crater. K. H. proposed the Earth-scale top model and assisted the paper.

Competing Interest Declaration

The authors declare no competing financial interests.

Additional Information

Supplementary Information The online version contains supplementary material available at www.nature.com/nature.

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Data availability

The data that support the findings of this study are available within this article and its Supplementary Information. Additional data are available from the corresponding authors on request.

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Figures

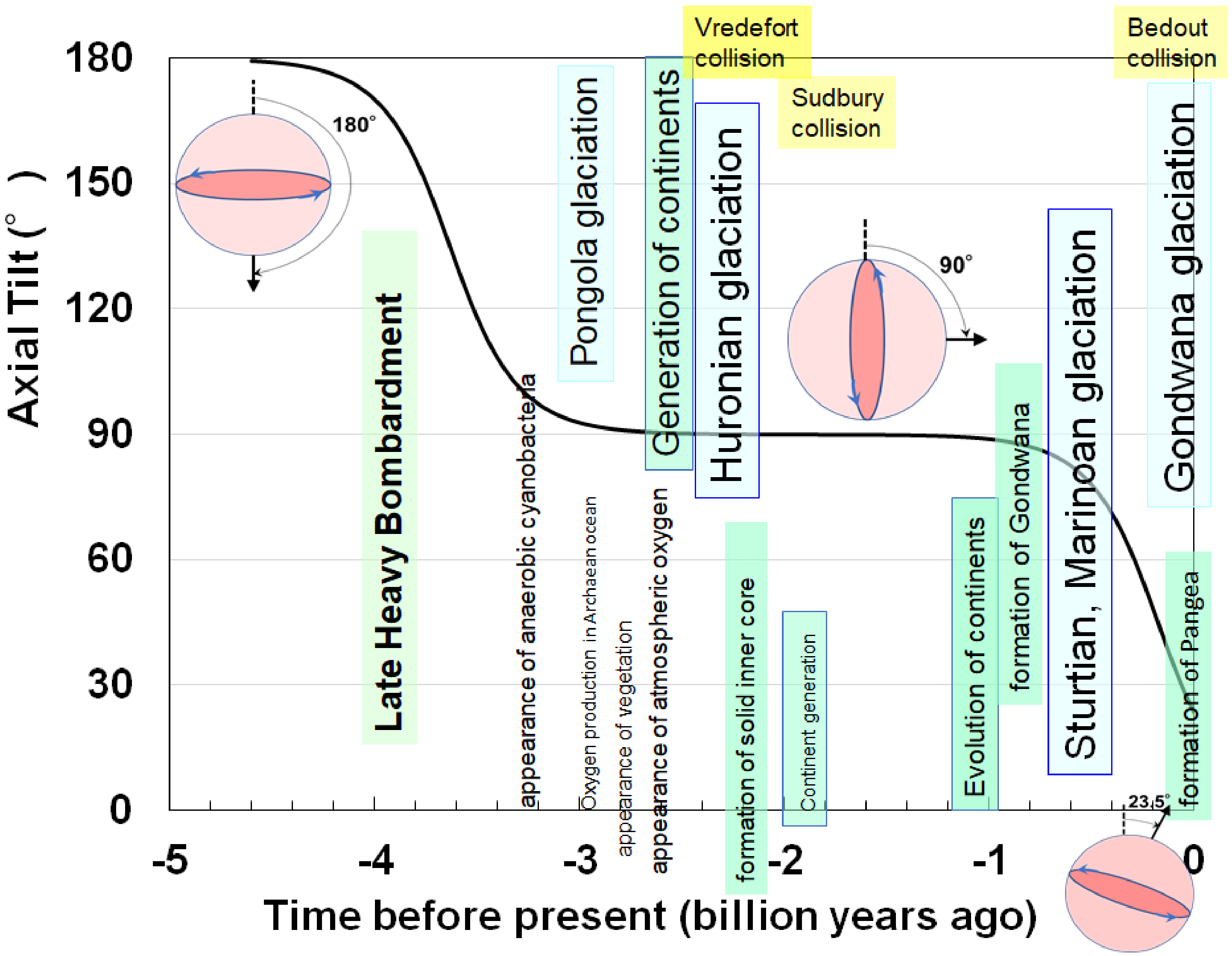

Figure 1

Changes in the axial tilt of Earth from billions years ago to the present time, along with historical geoscientific events. Earth with different axial tilts (180°, 90°, and 23.5°).

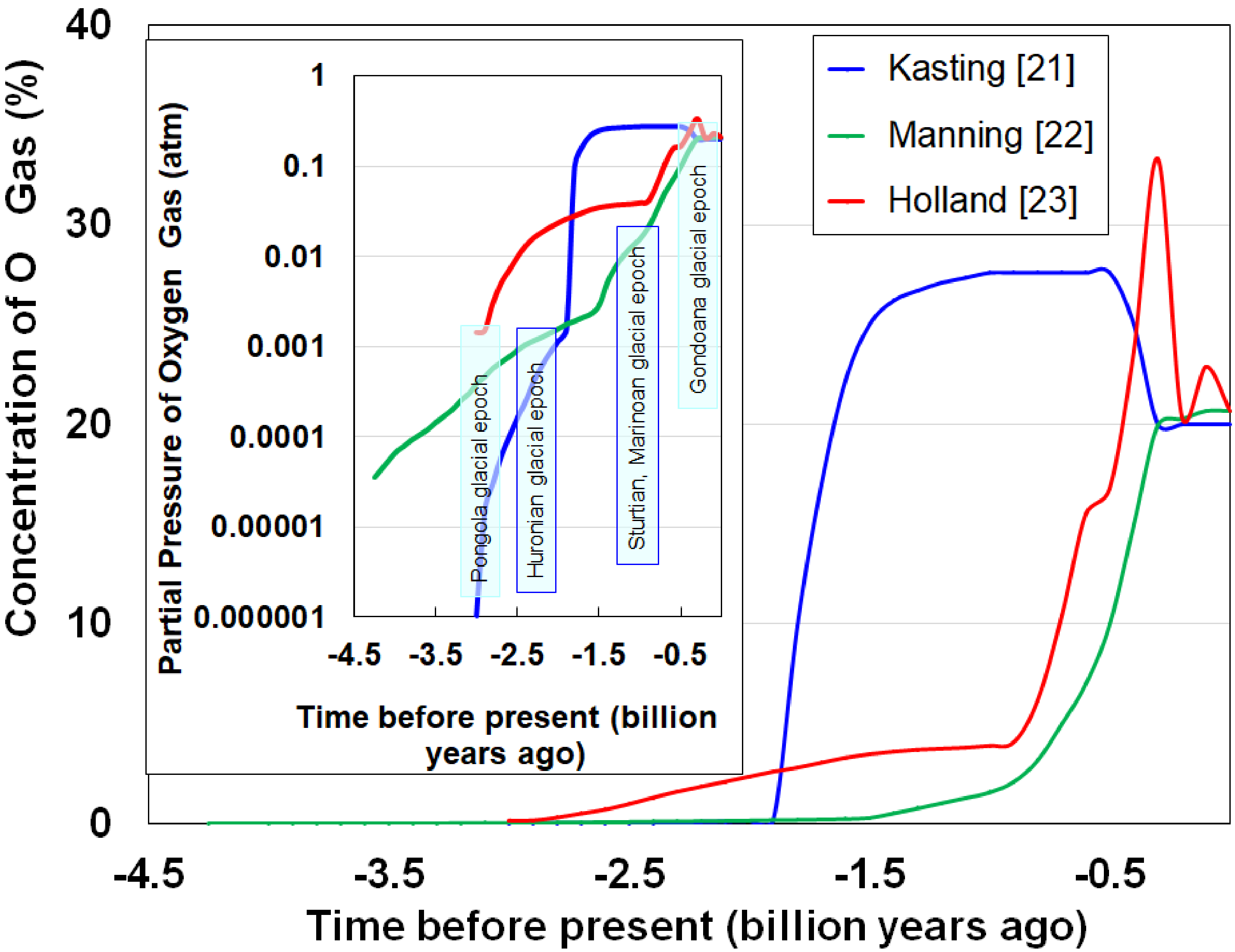

Figure 2

Changes in concentration of atmospheric O_2 from 4.5 billion years ago to the present time, using data obtained by three reserachers[21-23]. The inset shows a logarithmic plot of partial pressure of O_2 gas against time since 4.5 billion years ago. Four representative glacial periods correspond to rapid increases in partial pressure of oxygen gas.

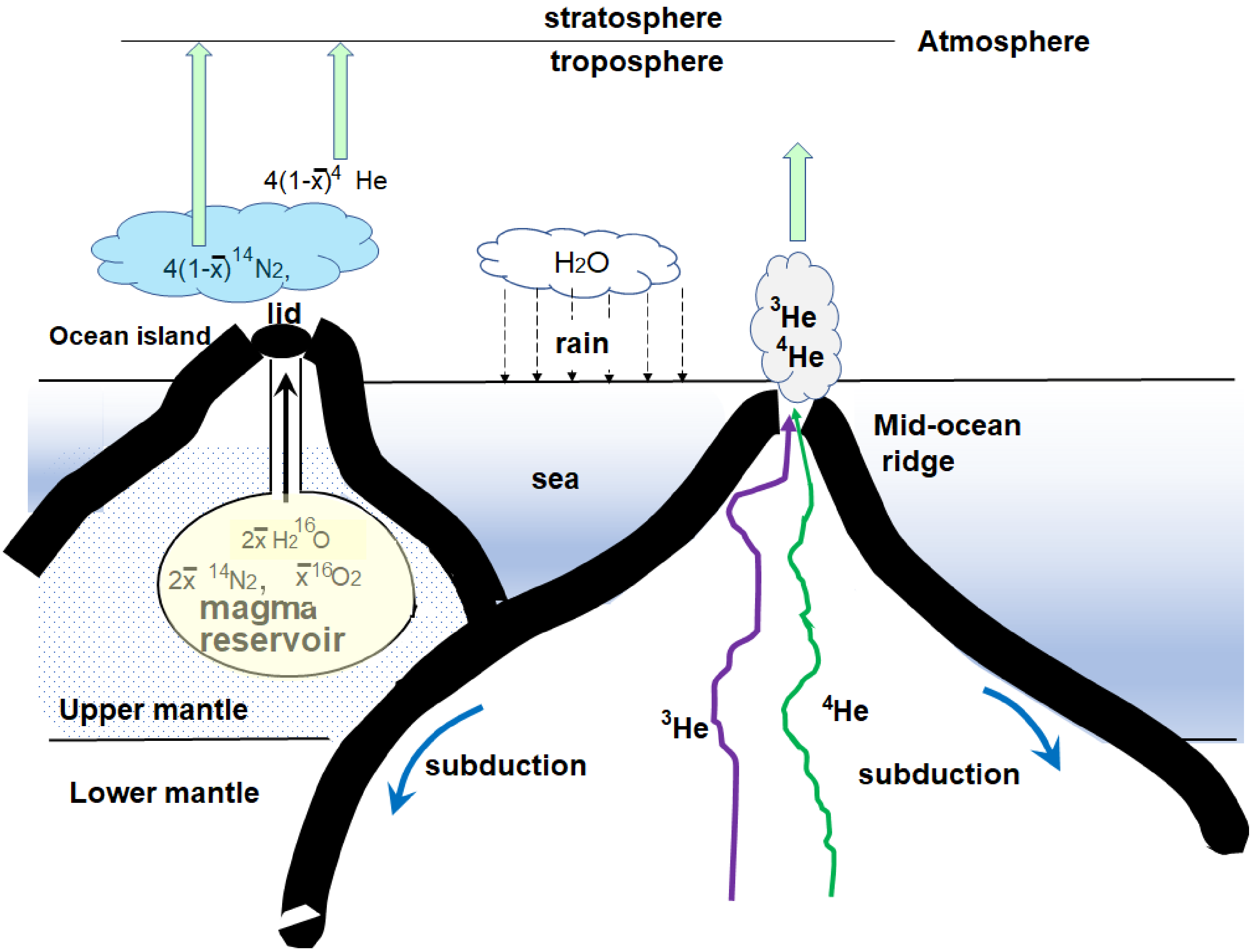

Figure 3

Schematic illustration of nuclei transformations in a magma reservoir of an ocean island and a middle ocean ridge. N_2, O_2, and H_2O are produced in the magma reservoir in the upper mantle, and ^{3}He and ^{4}He are formed from reservoirs of the lower mantle.

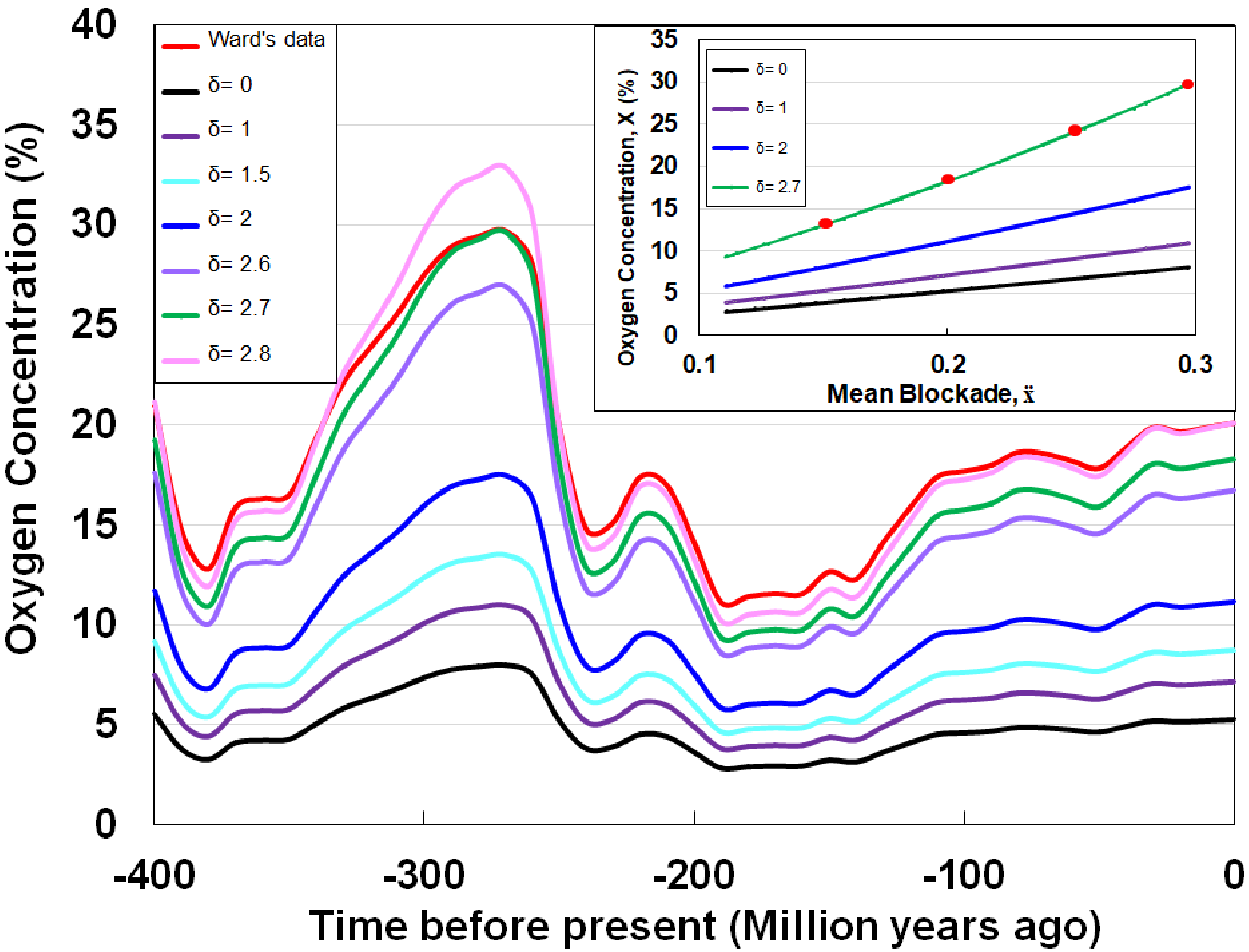

Figure 4

Relationship between atmospheric oxygen concentration, X, and nitrogen gas portion δ released into the stratosphere over the last 400 million years, which are obtained using a computational technique. Inset: Relationship between oxygen concentration, X, and the mean blockade of magma reservoirs, X¯ when δ=0, 1, 2, and 2.7. Four red closed circle are obtained from equation (7) at the values of δ=3 and α=0.27.

Supplementary Files

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- SupplementaryInformation.pdf