

Thermochemical equilibrium calculations of high-temperature O₂ generation on the early Earth: Giant asteroid impacts on land

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Abstract: Earth's atmosphere is composed primarily of N₂ and O₂. The origin of free O₂ in the early Earth's atmosphere is still subject of considerable debate.¹ Theoretical models suggest that the initial form of free O₂ in the atmosphere has been oceanic H₂O. Recent computation modelling has suggested that a superheated (*ca.* 2000 K) H₂O vapor atmosphere of 1.4×10^{21} kg (the present mass of the oceans) lasting for about 3000 y could probably have been formed on Earth by an enormous (*ca.* 10^{28} J) asteroid impact. In this report, the occurrence of the thermochemical dissociation of the vapor, creating a primitive oxygenic (*ca.* 0.1 of the present level (PAL) of free O₂) atmosphere.

Keywords: oxygen, atmosphere, thermochemistry, photochemistry, Earth, asteroid, impact.

INTRODUCTION

According to the current pedagogy the primitive Earth's atmosphere contained little or no free O₂. (The composition of the present-day atmosphere is unique within the solar system, consisting primarily of N₂ (*ca.* 78 % of the molecules in air), and aerobic life-sustaining O₂ accounts for *ca.* 21 %). More recent models hypothesize that the earliest atmosphere was probably formed by the accretion of extraterrestrial materials and by outgassing of the Earth's interior. As accretion diminished (*ca.* 4.4 Ga) and the Earth evolved, the superheated steamy atmosphere condensed to form ocean, leaving a neutral (primary) atmosphere dominated by CO₂ (*ca.* 1–10 bar), CO and N₂ (*ca.* 1 bar). (The neutral or weakly reducing primitive atmosphere was favorable for the emergence of anaerobic biota).¹

The fact that O₂ is present in considerable quantity (*ca.* 1.2×10^{21} kg) bound in the oceanic H₂O of today is evidence that much of the free atmospheric O₂ may be derived from this source. (The mass of O₂ in the present-day atmosphere is estimated to be *ca.* 1.2×10^{18} kg). It is generally agreed that the O₂ level increased markedly during the early Proterozoic. There are two (major) hypotheses that try to explain the origin of free O₂ in the

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early Earth's milieu: the first hypothesis, free O₂ was generated through microbial photosynthetic activity; second hypothesis, free O₂ was produced abiologically by photodissociation of atmospheric H₂O followed by escape of hydrogen (mainly as atomic H) to interplanetary space. Although the early atmospheric O₂ could have been created from the overall photodissociation reaction $\text{H}_2\text{O}(\text{g}) + h\nu (<200 \text{ nm}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$, this process was only capable of yielding small amounts of free O₂ (Kasting¹ and the references therein). Very recently, Premović and Panov² proposed that a high shock (pressure/temperature) decomposition of H₂O vapor derived mainly from the impacting icy comet in the ocean (or on land) could have been an alternative source of free O₂ in the early environment. (According to our model calculations, assuming a 100 % impact efficiency, a cometary impactor containing m kg of H₂O would generate approximately m kg of O₂).

Astronomical studies have suggested that the early Earth's surface should have been struck with a number of large/energetic asteroids. This resulted in the planet surface being heated to high temperatures, causing partial or complete evaporation of the early Earth ocean.³⁻⁷ Here I explore the hypothesis that such an impact could effectively generate free O₂ through thermal and/or photolytic dissociations of impact-related superheated H₂O vapor with subsequent escape of hydrogen into interplanetary space. Previous atmospheric studies ignored these possibilities.

PRE-BIOLOGICAL ATMOSPHERE

Very recently, Wilde *et al.*⁸ and Mojziz *et al.*⁹ reported U-Pb ages and oxygen isotopic compositions of *ca.* 4.4 Ga zircon grains. Their results provide evidence that continents and liquid H₂O were surface features of the earliest Earth. The definition of pre-biological Earth in this report covers the post-accretionary period (after *ca.* 4.5 Ga) in the early geologic history to about 3.8 Ga (the early Archean). The model of a pre-biological Earth presented here is with an atmosphere dominated by CO₂ (up to 10 bars), and with a planet's surface temperature of about 273 K. (The mean temperatures of the early Archean ocean may have been as high as 420 K).¹⁰

Sleep *et al.*^{3,4} have proposed that the early Earth (prior to 3.8 Ga) was struck several times by extraterrestrial objects with impact energies (*ca.* 10²⁸ J) sufficient to evaporize the entire early ocean. According to these authors, such immense impacts resulted in the formation of a global 100 bar rock-vapor atmosphere, which persists for several months before cooling/condensation. During this time, the entire ocean is evaporated, maintaining the surface temperature to *ca.* 2000 K for about 3000 years. The mass of H₂O contained in the oceans is estimated to be 1.4 × 10²¹ kg, corresponding to a globally average surface pressure of *ca.* 270 bar. Note that under these conditions (above the critical point: > 221 bar and > 647 K) H₂O behaves as a supercritical fluid which may greatly influence many geochemical/atmospheric processes.¹¹ We can reasonably consider that the temporary impact-induced atmosphere (IIA) (originating from an impact-induced evaporation of the entire ocean) is composed principally of H₂O vapor and a relatively minor CO₂ (*ca.* 10 bar), neglecting the possible contribution of the other gases. For the following discussion, I make the reasonable assumption that in the early Earth there has been about as much H₂O in the ocean as we as-

sumed to be present today. (I neglect the H₂O vapor escape driven by the impact and a fraction of H₂O vapor which is dissolved in the surface rocks molten by the impact-induced heating). I also assume that the impacting large asteroid is ordinary and enstatite chondrite from the innermost of the asteroid belt, containing a very low amount of H₂O.⁷

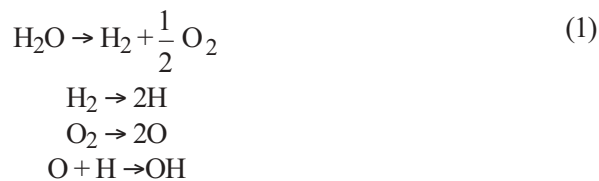
THE H₂O/O₂ INVENTORY: A BIOLOGICAL MINIMUM OF FREE O₂

Paleontological studies of Archean microfossils and stromatolites^{12,13} and carbon isotopic studies¹⁴ show that life may already have existed by 3.8 Ga. Recently, Han and Runegar¹⁵ reported finding megascopic eukaryotic (photosynthetic) algae, tentatively identified as *Grypania spiralis*, in the 2.1 Ga old rocks. They suggested that these microfossils are an indication that the Earth's atmosphere as well as the surface ocean between 2.0 and 2.5 Ga contained at 0.01 – 0.1 PAL of free O₂. Note that 0.01 PAL is “the Pasteur point” or “the first critical level of O₂” (Barkner and Marshall¹⁶ and references therein). Such biologically based estimates are adopted, for purposes of the following calculations, as useful values for the levels of free O₂ in the early atmosphere. If the small amount (10⁻³ PAL, for example) of this gas is suddenly added to the primitive atmosphere and ocean, it would have a profound (mainly toxic) effect on the anaerobic biota. (Note that the model calculations predict that a biologically effective O₃ layer is established at 0.01 to 0.1 PAL of free O₂: Kasting¹ and the references therein). Assuming that the impact-related H₂O vapor (decomposed through the photochemical process and/or thermal process) is completely converted into O₂, simple arithmetic reveals that the 1.4 × 10¹⁵ kg (*i.e.*, 1 ppm) fraction of the entirely evaporized ocean would generate an atmosphere with 10⁻³ PAL of free O₂. It appears, thus, that the hypothesis of an early (oxygenic) atmosphere seems, therefore, to require an entirely small amount of thermally and/or photochemically decomposed H₂O vapor generated by a giant asteroid impact.

THERMAL DISSOCIATION OF H₂O VAPOR

The H₂O vapor dissociation has an activation energy threshold of *ca.* 31 MJ kg⁻¹. H and O are formed and then recombine to H₂ and O₂, losing about 18 MJ kg⁻¹ in the recombination reaction. The chemical reactions associated with high temperatures dissociations of H₂O vapor are shown below, along with their pressure equilibrium constants.

Chemical reactions:



Pressure equilibrium constants:

$$K_1 = P^{\frac{1}{2}} \cdot \frac{[m(\text{H}_2)]^2 \cdot m(\text{O}_2)]^{\frac{1}{2}}}{m(\text{H}_2\text{O})} \quad K_2 = P \cdot \frac{[m(\text{H})]^2}{m(\text{H}_2)}$$

$$K_3 = P \cdot \frac{[m(\text{O})]^2}{m(\text{O}_2)} \qquad K_4 = \frac{1}{P} \cdot \frac{m(\text{OH})}{m(\text{O}) \cdot m(\text{H})}$$

(Where P is the total pressure and $m(x)$ is the mole fraction of the corresponding species x).

Mole fraction equation:

$$m(\text{H}_2\text{O}) + m(\text{O}_2) + m(\text{H}_2) + m(\text{H}) + m(\text{O}) + m(\text{OH}) = 1$$

Eq. 1 is, of course, an over-simplification of the primary reaction, because the third body (M) reactions (*e.g.*, $\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$) in this case are probably significant.

Thermochemical equilibrium calculations were done using the Gibbs-free-energy-minimization method (the STANJAN method) and JANAF thermochemical tables (the Chemkin collections[®]).¹⁷ The results of the calculations are shown in Fig. 1. At low temperatures (*ca.* < 1500 K), H_2O vapor (steam) does not dissociate, and chemical reactions can be neglected. At high temperatures (*ca.* > 1800 K), the H_2O vapor begins to dissociate into a mixture of H_2O and O_2 , H_2 , O , H and OH .^{2,18} Figure 1 shows the mole fractions of H_2O (a, b), O_2 (c, d), O (e, f), H_2 (g, h), H (i, j) and OH (k, l) at different temperatures (from 1500 K up to 3500 K) and different pressures (from 1 mbar up to 270 bar). Figs. 1a/b show that H_2O vapor is < 1 % dissociated at temperatures ≤ 2000 K and at pressures ≥ 1 bar (*i.e.*, in the homosphere), and that at temperature > 2000 K up to 3500 K and at pressures < 1 bar (*i.e.*, in the thermosphere) > 1 % of H_2O is decomposed.

Thermochemical equilibrium calculations also show that generation of O_2 from H_2O vapor at temperatures < 3500 K is significantly affected by the abundance of hydrogen, Fig. 1. These calculations over a wide range of assumed compositions of this vapor show that the speciation in the vapor depends on the bulk H/O ratio. In the hydrogen-enriched vapor H_2O would be the major gaseous component and in the hydrogen-depleted vapor O_2 would be the major species. Thus, a high H/O ratio would suppress thermochemical formation of O_2 within the superheated vapor and a low H/O ratio would favor this process. For this reason, of crucial importance for thermal generation of O_2 in H_2O vapor is the removal of hydrogen from the system. This removal would keep hydrogen from re-reacting with O_2 , making ultimately H_2O again. In this case hydrogen could be separated from O_2 by the escape.

VERTICAL STRUCTURE OF THE STEAM PROTO-ATMOSPHERE

Assuming a plane-parallel IIA (with $P = Mg/4\pi R^2$, where M is the corresponding atmospheric mass), elementary hydrostatics shows that the pressure (P) of the H_2O vapor in IIA diminishes with height according to formula

$$P = P_0 \times e^{-h/H_s}$$

where h is the altitude above the surface where the pressure is P_0 . The scale height is given by

$$H_s = RT/1.8 \times 10^{-2} g$$

where R is the gas constant (8.3 J K⁻¹). The result of the above formula applies to a region

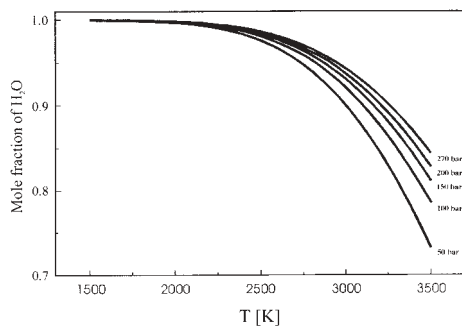
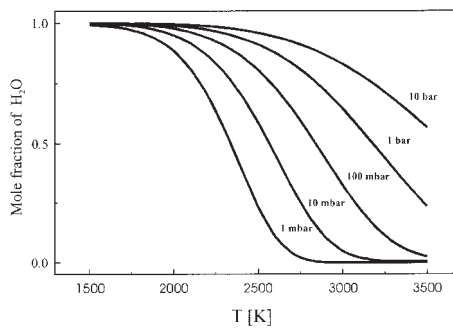
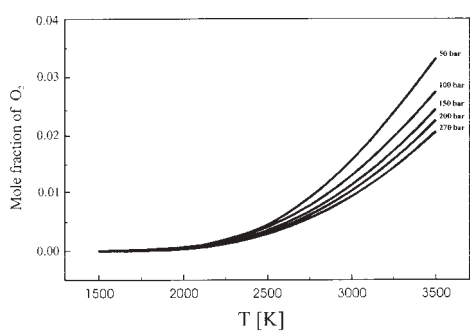
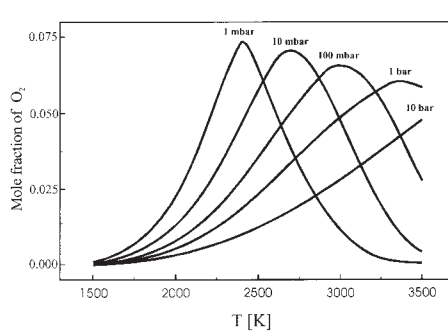
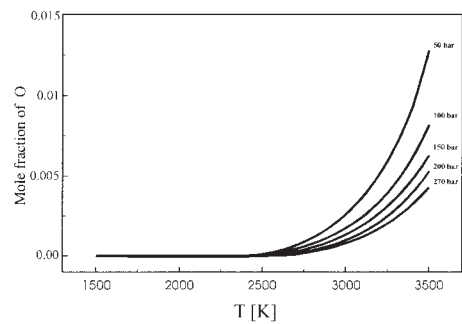
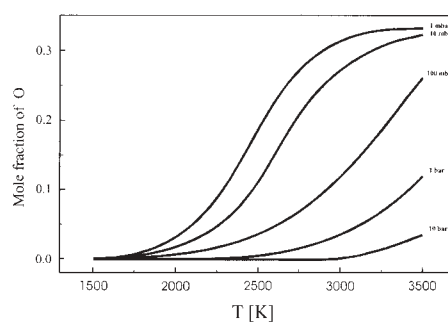
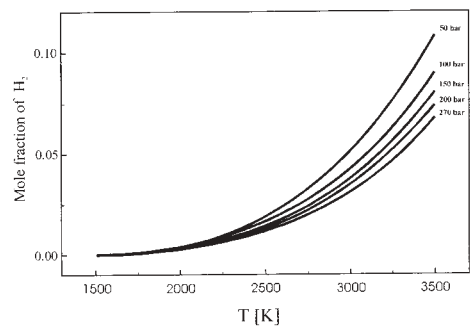
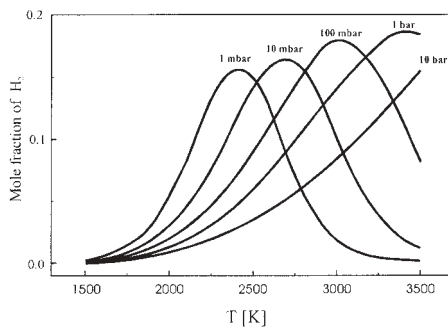
in which temperature T and the gravitational acceleration g is constant. I assume that fractional variations in temperatures are relatively small ($\leq \pm 20\%$), so H_S is roughly constant with a value of about 97 km. (Typically, $g = 9.8 \text{ m s}^{-2}$: at sea-level, $g = 9.5 \text{ m s}^{-2}$: at $h = 100 \text{ km}$, $g = 9.2 \text{ m s}^{-2}$: at $h = 200 \text{ km}$, $g = 9.0 \text{ m s}^{-2}$: at $h = 300 \text{ km}$, $g = 8.9 \text{ m s}^{-2}$: at $h = 400 \text{ km}$ and $g = 8.5 \text{ m s}^{-2}$: at $h = 500 \text{ km}$).

The accurate structural model of IIA is a complex issue and, of course, beyond the scope of this paper. (The present-day atmosphere is divided into four main concentric spherical strata: *e.g.*, troposphere, stratosphere, mesosphere and thermosphere). For simplicity, I divide the superheated steam IIA into only two main regions primarily on the basis of temperature gradient. The thermal H₂O dissociation profile for IIA is displayed in Fig. 2. A zone above the surface is isothermal ($T \approx 2000 \text{ K}$) and uniform in composition. This zone is termed homosphere. H₂O vapor in the homosphere is well mixed by turbulence. (A “cold trap”, such as that which confines H₂O to the present-day troposphere,¹⁹ does not exist in IIA). The homosphere extends roughly 550 km above the ocean-level and more than 99 % of the mass of IIA is concentrated in it. Above the homosphere, in the thermosphere, temperature increases with altitude, reaching a value of $> 2000 \text{ K}$ mainly through heating by solar UV radiation. The exosphere is a transitional zone between IIA and interplanetary space and its temperature is high (far above 2500 K) enough to permit hydrogen to escape as fast as it is produced. The temperature of the today’s exosphere is as high as *ca.* 1300 K and throughout the history of our planet most of hydrogen has escaped through the exosphere, while O₂ has remained.

THE HYDROGEN ESCAPE

The amount of hydrogen present is determined by the balance between the sources and the escapes for hydrogen. In general, the loss of hydrogen to interplanetary space is determined by the diffusion to the exosphere. If all hydrogen is eventually lost to space, the population gradient of hydrogen in the underlying layers would adjust to a level that supports a loss rate to interplanetary region that is equal to the rate of input by diffusion, making diffusion limiting factor in the establishment of a loss rate. The rate of loss of hydrogen is, therefore, limited to the rate at which hydrogen is transported upwards from lower layers.²⁰ The mole fraction of hydrogen in the present-day stratosphere and the above is controlled by the “cold trap” and is *ca.* 13 ppm. (The cold trap only begins to limit the abundance of hydrogen in the upper levels of the today’s atmosphere when the H₂O mixing ratio falls below 0.1).²¹ The rate of the hydrogen escape from the present-day Earth is limited to about $2.7 \times 10^8 \text{ atoms cm}^{-2} \text{ s}^{-1}$ by the ability of the H₂O vapor to penetrate cold trap of the stratosphere and reach high enough altitudes to be photodecomposed, and by the ability of hydrogen to diffuse upward to the exosphere. The present rate of the hydrogen escape is so small that the present H₂O inventory could not be depleted by more than 0.01 % over the age of the Earth (*ca.* 4.5 – 4.6 Ga).

In the following discussion, I shall consider a model of thermal and/or photolytic decompositions of the H₂O vapor in IIA at a constant rate continued for 3000 y.

a)**b)****c)****d)****e)****f)****g)****h)**

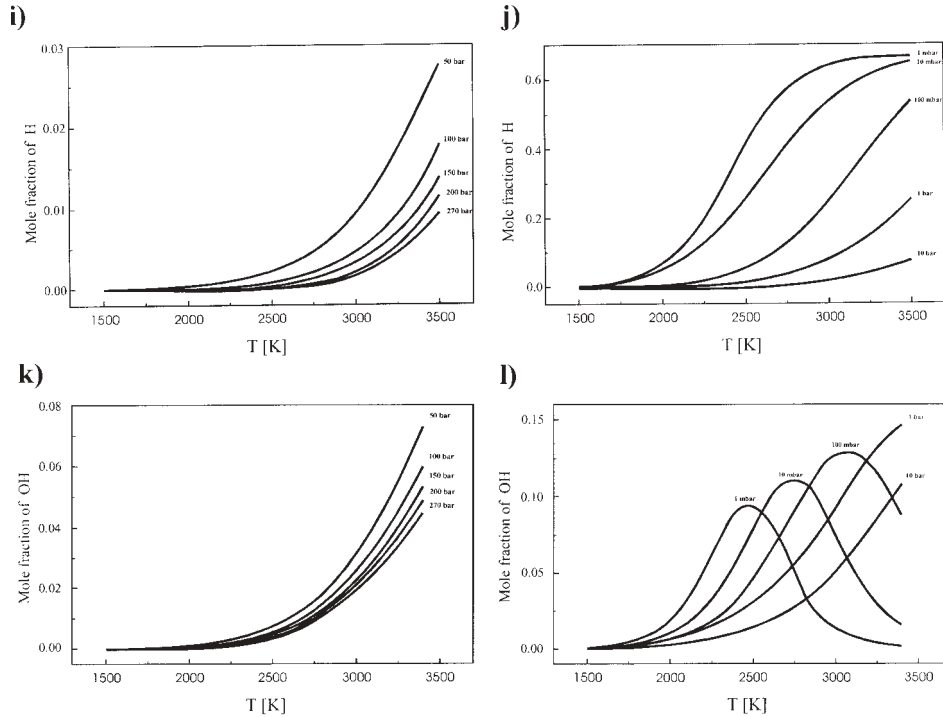


Fig. 1. Thermochemical equilibrium abundances of H₂O (a, b), O₂ (c, d), O (e, f), H₂ (g, h), H (i, j) and OH (k, l), as a function of temperature (from 1500 K up to 3500 K) and a constant pressure (from 1 mbar up to 270 bar).

ESCAPE OF HYDROGEN AND GENERATION OF FREE O₂

The escape of hydrogen from the steam primitive atmosphere of a model-planet (Venus/Earth) with the terrestrial ocean of H₂O has been examined by Walker,²¹ McElroy and Hunten,²² Smith and Gross²³ and Hunten.²⁴ They found that exospheric temperatures high enough (> 1000 K) permit hydrogen to escape essentially as fast as it was generated. As H₂O vapor is a major constituent at all levels of IIA, then it is one of the principal absorbing gases of ultraviolet UV sunlight. The average solar flux of photons available at the today's Earth whose energy is above the dissociation limit of H₂O is about 10^{13} photons $\text{cm}^{-2} \text{s}^{-1}$.²⁰ If the present solar flux is assumed to be true for the pre-biological Earth, no more than 2×10^{13} hydrogen atoms $\text{cm}^{-2} \text{s}^{-1}$ can be generated and escape IIA. At this rate (which corresponds to the decomposition of *ca.* 4.8×10^{13} kg y^{-1} of H₂O), about 1.45×10^{17} kg of the superheated H₂O vapor of IIA dissociates for 3000 y or approximately 1×10^{-2} % or 100 ppm of its total H₂O. Thus, after 3000 y H₂O vapor in IIA is photochemically converted to about 1.3×10^{17} kg (*i.e.*, *ca.* 0.1 PAL) of O₂ followed by escape of hydrogen. This is a maximum estimate because the rate of the hydrogen escape may be reduced by a number of factors. For example, theories of the Sun's interior predict that its UV flux increased by 30 % over the past 4.6 Ga.

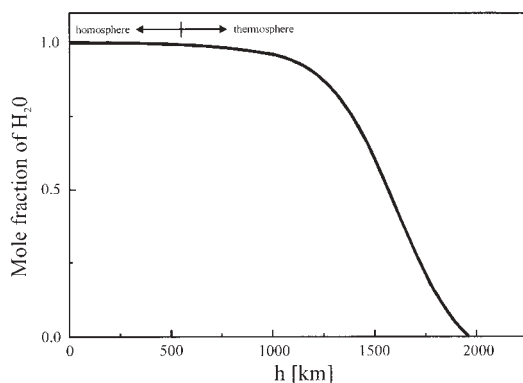


Fig. 2. Thermochemical abundance of H_2O as a function of the altitude: up to 550 km (homosphere) and above 550 km (thermosphere).

The dissociation equilibrium of H_2O vapor at temperatures < 2000 K and pressure of 1 bar is reached within about 10^{-3} s (Jelinek¹⁸ and the references therein). With the present data, simple thermochemistry shows that the thermal decomposition of H_2O vapor in IIA occurs at a rate of about 10^{29} molecules $\text{cm}^{-2} \text{s}^{-1}$ averaged on the planet surface. When this figure is compared with the rate of photochemical dissociation (*ca.* 10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$) of the IIA vapor, one finds that the rate of the thermochemical process greatly overwhelms its photochemical analogue. In other words, I suggest that most of free O_2 in IIA is mainly produced by thermodissociation of its H_2O vapor. If we assume that the rate of escape of hydrogen in IIA is limited by upward transport,^{21,24} as in the modern atmosphere, then the escape flux of hydrogen would be about 2×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$. By the same reasoning as before, approximately 1.45×10^{17} kg of superheated steam would be thermally decomposed for 3000 y, generating about 1.3×10^{17} kg (*ca.* 0.1 PAL) of free O_2 , followed by escape of hydrogen.

Free O_2 in IIA is partly consumed by oxidation of the reducing (molten) surface rock minerals and reducing volcanic gases (mainly H_2 , CO , SO_2 and reducing fluids from the oceanic hydrothermal vents).²⁵ Geochemical studies, however, indicate that the surface oxidation (which may be written schematically as $2\text{Fe} + 3/2 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$) was minimal during the Archean, leaving reducing volcanic volatiles as a major free O_2 sink.²⁵ According to these authors, the total volcanic sink rate for free O_2 is about 4×10^{10} kg y^{-1} . After 3000 y, therefore, approximately only 1.2×10^{14} kg (about 1 ppm) of O_2 in IIA could be consumed by the volcanic sink.

On subsequent cooling, H_2O vapor in IIA condenses back to a primitive ocean. After the cooling/condensation stage is completed free O_2 in IIA has a partial pressure of *ca.* 40 mbar. Thus, I suggest that an unspecified part of the present free O_2 could be a residual from O_2 generated by an enormous asteroid impact on the early Earth's surface. Sleep *et al.*^{3,4} have suggested that the early ocean could have been repeatedly evaporized by the enormous impacts. Chyba *et al.*²⁶ estimated that Earth should sustain about 5 such enormous impacts between 4.4 Ga and 3.8 Ga. This implies that free O_2 may rise in the primi-

tive atmosphere in few great bursts and not gradually. On the other hand, these impacts may cause periodic formation and erosion of early atmosphere and ocean, implying that the impact-induced generation of free O₂ on the early Earth may have occurred more than once, at least, before *ca.* 3.8 Ga. (Impact erosion is the explosive removal of a portion of the atmosphere/hydrosphere by a large impact). Thus, enormous impacts are consistent with periodic destruction and formation of early oxygenic atmosphere and ocean. (This implies that primitive oxygenic life, if it evolved in the early ocean, was globally extinguished more than once). Conceivably, a large cometary impact on land or into ocean would generate a much higher amount of free O₂ in the early atmosphere, compared with an enormous asteroid impactor with similar mass and speed. (This additional free O₂ would be created by the cometary H₂O vapor).

Sleep *et al.*^{3,4} also propose that an impacting (at 17 km s⁻¹) high-energy (*ca.* 10²⁸ J) asteroid with a mass of 1.3 × 10²⁰ kg is needed to evaporate the entire ocean. If this impactor was a hydrated carbonaceous chondrite from the outer asteroid belt then it could contain as much as 10 % (in mass) of H₂O.⁷ Assuming a 100 % efficiency in the impact decomposition of H₂O associated with a carbonaceous chondrite (say, containing about 1–10 % of H₂O), it turns out that 1–10 PAL of free O₂ could have been created in the primitive atmosphere. (Note that the levels of free O₂ in the atmosphere above about 1.4 PAL would cause the formation of toxic oxygen radicals that damage cell structure and function of aerobic biota).

FREE O₂ AND AEROBIC BIOTA

The existence of free O₂ in primitive atmosphere could have important implications for the evolution of photosynthetic aerobic microorganisms. If we take arbitrarily 0.01 PAL of free O₂ as a basis for estimating when the photosynthetic generation of free O₂ begins, I find that only 10⁻³ % (*i.e.*, 10 ppm) of H₂O vapor in IIA is enough to be decomposed into free O₂. As free O₂ accumulated after the advent of photosynthetic oxygenic microbiota, conditions would approach closer and closer to those of today. (For many forms of anaerobic microbiota, the concentration of free O₂ in the primitive atmosphere and ocean is the most critical in their living environment). It is possible that primitive aerobic microbiota may have helped prepare the way for the advent of more complex green plants on the Earth. In addition, when the O₂ level in IIA advances to about 0.1 PAL a powerful O₃ screen starts to form in the upper atmospheric layers. The presence of atmospheric O₃ is essential to the existence of most plant/animal biota since O₃ is the only important absorber of solar near-UV radiation between 2000 and 3000 Å.

CONCLUSIONS

In this paper I have shown that generation of (*ca.* 0.1 PAL) free O₂ occurs in a superheated H₂O steam atmosphere created by a large asteroid impact during the early geologic history of Earth. This process could have occurred through mainly thermochemical dissociation of H₂O vapor followed with escape of hydrogen to space. I have suggested that an

initial supply of free O₂, sufficient to support aerobic microbiota and permit oxygenic photosynthesis, may have been produced by the above process.

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ИЗВОД

ТЕРМОХЕМИЈСКА РАВНОТЕЖНА ИЗРАЧУНАВАЊА
ВИСОКО-ТЕМПЕРАТУРНОГ НАСТАЈАЊА O₂ НА РАНОЈ ЗЕМЉИ: УДАР
ГИГАНТСКОГ АСТЕРОИДА НА КОПНО

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Земљина атмосфера је састављена углавном од N₂ и O₂. Порекло слободног O₂ у првобитној атмосфери је још предмет значајне дебате.¹ Теоретски модели указују да је почетни облик слободног O₂ у атмосфери била океанска H₂O. Савремена компјутерска моделирања указују да је удар огромног (око 10²⁸ J) астероида формирао атмосферу прегрејане (око 2000 K) водене паре масе 1,4 × 10²¹ kg (тренутна маса океана), која се одржала на Земљи за око 3000 година. Показано је да је могло да дође до термохемијске дисоцијације суперпрегрејане паре стварајући примитивну кисеоничну атмосферу (са око 0,1 садашњег нивоа (PAL) слободног O₂).

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