Cometary Impacts into Ocean: Thermochemical Equilibrium Calculations of High-Temperature O_2 Generation on the Early Earth

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Abstract

The early Earth's atmosphere apparently differed from the present atmosphere mainly by its lack of free O_2, a condition that is believed to have been indispensable for the origin of early anaerobic life forms. One of the central problems in Earth science is to explain the apparent transition from a primitive atmosphere (free of O_2) to the present atmosphere which holds 21 % of the gas. Theoretical models suggest that the initial form of O_2 in Earth's atmosphere may have been H_2O, which was converted into atmospheric O_2 mainly through photosynthesis. I have investigated an alternative (abiotic) method for converting H_2O to O_2: a high temperature shock generated during the cometary impact into ocean (or on land). Calculations show that 1 % of the present atmospheric level (PAL) of O_2 could have resulted from an icy 29.2 km comet impacting the early (pre-oxygenic) Earth with a velocity between 18 and 37 km s^{-1}. It is suggested that an abrupt supply (10^{-2} % of PAL) of free O_2 by the comet would be sufficient to make way for the appearance of oxygenic photosynthetic microorganisms.

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1. Introduction

A distinctive feature of Earth is the large amount of free O_2, 21 % by volume, in the atmosphere. Because volcanic exhalations at present lack free O_2, only two principal sources of atmospheric O_2 have been considered plausible: a biological source localised in the ocean, producing O_2 *via* photosynthesis and an abiological source localised in the atmosphere, generating O_2 *via* photodissociation of H_2O vapor. Model calculations predict that the production rate of O_2 from photodissociation of H_2O vapor would have been relatively small on the early Earth (Kasting [1] and references therein). According to the current thinking, anoxygenic (bacterial) photosynthesis existed by the early Archean (ca. 3.8 Ga). Oxygenic phototsynthesis (cyanobacteria) began producing free O_2 prior to middle Archean (ca. 3.5 Ga) and current O_2 level was reached about 1.5 Ga ago [2].

Very recently, Wilde, *et al.* [3] and Mojzsis, *et al.* [4] reported U-Pb ages and oxygen isotopic compositions of ca. 4.4 Ga zircon grains. Their results provide evidence that continents and liquid H_2O were surface features of the earliest Earth. H_2O appeared on Earth very early in its history. Studies indicate that H_2O came from the outer solar system, supplied by chondrites and comets colliding with the newly-formed planet [5-7]. According to Morbidelli, *et al.* [7], after the Earth's formation ended, its surface was impacted by comets. This was a late veneer phase, coinciding with the late heavy bombardment from 4.4 to at least, 3.8 Ga.

The definition of pre-oxygenic Earth here encompasses the time period (Hadean/Archean eras) in the early Earth geologic history from about 4.4 Ga (after its main accretion phase following core-segregation and formation of ocean) up to 2.2 Ga (the early Proterozoic). The model of a pre-oxygenic Earth presented here has no or little atmosphere, and the planet's surface temperature is ca. 273 K.

The following preliminary report concentrates first on thermochemical equilibrium calculations of thermally decomposed H_2O vapor, second on a specific application of these calculations to an oceanic cometary impact, and third on the O_2 generation from thermally disintegrated H_2O vapor within the expanding plume created by the impact.

2. Cometary Impact into Ocean

I explore here a possibility that during a cometary impact into an ocean the cometary ice-H_2O could have been exposed to an impact-induced (high-temperature) decomposition, generating O_2. Previous studies of such impacts have ignored this possibility, and failed to estimate the amount of O_2 which could be formed in such an event. For this purpose, I have carried out theoretical calculations using the Gibbs-free-energy-minimization method (the STANJAN method) and JANAF thermochemical tables (the Chemkin collections®)[8].

Emphasis is placed here on an oceanic impact of an ice-rich comet because: (a) the number of Earth crossing comets is four times greater than the number of Earth crossing asteroids [9]; (b) probability arguments indicate that ca. 70 % of the impactor flux would land in the ocean, being substantially higher (>80%) during the Archean period [10]; (c) the impact-decomposed oceanic H_2O could enhance the abundance of H_2O vapor in the initial plume (at the moment of impact); and (d) impact-generated H_2O vapor derived from the cometary and impacted H_2O could reach a temperature of tens of thousands of degrees or even higher [11-16].

I assume that the O_2 generation by the cometary impact into the pre-oxygenic Earth ocean took place in two major steps. The first one includes the disintegration of cometary H_2O vapor at high temperatures (20,000 K) into molecular oxygen (O_2) and hydrogen (H_2). The second step comprises the escape of H_2 into interplanetary space.

3. Thermal Decomposition of H_2O

The chemical reactions associated with the decomposition of H_2O vapor (at temperatures <6000 K and at pressures <1 bar) are shown below,

$$H_2O \rightarrow H_2 + 1/2O_2 \qquad (1)$$

$$H_2 \rightarrow 2H$$

$$O_2 \rightarrow 2O$$

$$O + H \rightarrow OH$$
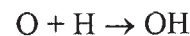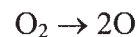
along with their pressure equilibrium constants

$$K_1 = f(H_2) [P f(O_2)]^{1/2} [f(H_2O)]^{-1}$$

$$K_2 = P [f(H)]^2 [f(H_2)]^{-1}$$

$$K_3 = P [f(O)]^2 [f(O_2)]^{-1}$$

$$K_4 = f(OH) [P f(O) f(H)]^{-1}$$

and the mole fraction equation

$$f(H_2O) + f(O_2) + f(O) + f(OH) + f(H_2) + f(H) = 1$$

where P is the total pressure and f (X) is the mole fraction of the gaseous component X. (The mole fraction of the different gases are equal to the partial pressure of a gas divided by the total

pressure. The mole fraction of O_2 in dry air is 0.21). Reaction (1) requires a substantial amount of energy (ca. 245 kJ) to produce gaseous H_2 and O_2 and the above process is endothermic, i.e., high temperatures and low pressures favor decomposition of H_2O vapor. (H_2O vapor dissociation has an activation energy threshold of about 31 MJ kg^{-1}. O and H are formed and then recombined to O_2 and H_2, losing about 18 MJ kg^{-1} in the recombination process). Eqn. (1) is, of course, an over-simplification of the primary reaction, because third body (M) reactions (e. g. $H_2O + M \rightarrow H + OH + M$) in this case are probably significant.

Many authors studied the decomposition of H_2O vapor (steam) by direct thermolysis (as summarized by Fletcher and Moen [17], King [18] and Jellinek [19]) and by shock (Bauer, *et al.* [20] and Lyzenga, *et al.* [21] and references therein). Available experimental data indicate that at low temperatures, H_2O vapor does not decompose, but at high temperatures (>1500 K), dissociation becomes significant. These investigations also show that the most abundant species generated during the decomposition are O_2, H_2, O, H and OH and that the extent of dissociation, as expected, increases with increasing temperatures and decreasing pressure. (The decomposition of H_2O vapor resulting from the high-temperature (>3000 K) heating under atmospheric pressure (1 bar) or higher pressures has not yet been studied).

4. Thermochemical Equilibrium Calculations

Equilibrium thermochemical calculations show that thermal decomposition of H_2O typically takes place at temperatures above 1500 K which agrees with expectations based on previous experimental results (for the details, see Fletcher and Moen [17], King [18] and Jellinek [19]). The equilibrium abundances of H_2O at different temperatures (up to 3500 K) are illustrated in Fig. 1: at 0.2 mbar, 2 mbar and 20 mbar; and, for comparison, the mole fractions of H_2O at 1 bar (present-day atmospheric pressure) and at 270 bar. (The oceans contain ca. 1.4×10^{21} kg of H_2O, corresponding to a globally averaged surface pressure of 270 bar). Fig. 2 shows the chemical equilibrium abundances of O_2 as a function of temperature (up to 5000 K) at 0.2 mbar, 2 mbar, 20 mbar, 1 bar and 270 bar. (Similar results were obtained by a simulation based on the polarization model for H_2O and by the reaction progress variable method). It should be noted that above the critical point (>221 bar and >647 K) H_2O behaves as a supercritical fluid which may greatly influence many chemical processes in the plume [22].

As shown in Fig. 2, the maximum O_2 abundances (ca. 7-8 %) at 0.2 mbar, 2 mbar and 20 mbar were generated at about 2100 K, 2400 K, 2700 K, respectively. The equilibrium abundance of O_2 decreases at higher temperatures (up to 5000 K) because most of the O_2 is converted to O and OH.
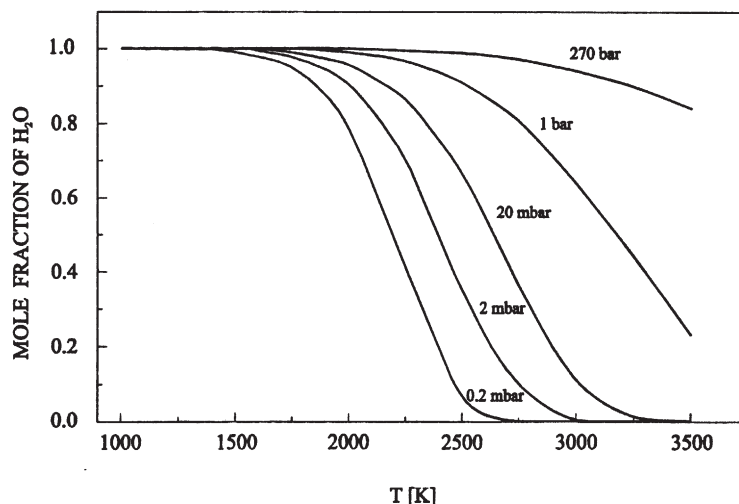

Fig. 1. Thermochemical equilibrium abundances of H_2O as a function of temperature (up to 3500 K) and a constant pressure (0.2 mbar, 2 mbar, 20 mbar, 1 bar and 270 bar).
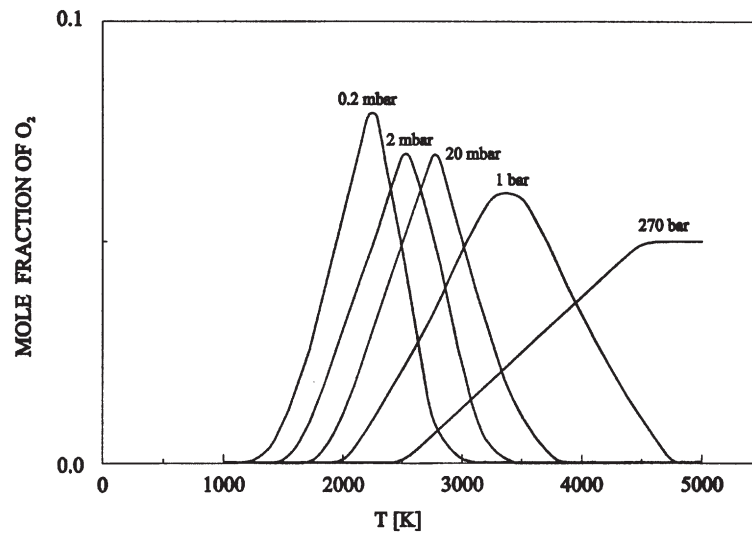
Fig. 2. Thermochemical equilibrium abundances of O_2 as a function of temperature (up to 5000 K) and a constant pressure (0.2 mbar, 2 mbar, 20 mbar, 1 bar and 270 bar).

5. Impact-Induced Decomposition of H_2O Vapor

Paleontological studies of Archean microfossils and stromatolites [23,24] and carbon isotopic studies [25] show that life may already have existed by 3.8 Ga. Very recently, Han and Runnegar [26] report finding eukaryotic microfossils, tentatively identified as *Grypania spiralis*, in 2.1 Ga old rocks. The authors claim that the atmosphere of Earth between 2.0 and 2.5 Ga contained 0.01 to 0.1 PAL of O_2. (The mass of O_2 in the present-day atmosphere is estimated to be ca. 1.2×10^{18} kg). I consider that such biologically based estimates provide useful minimum values for the early oxygenic Earth and, for purposes of the following calculations, the value of 0.01 PAL O_2 has been adopted.

Using numerical data from Pierazzo and Melosh [13], O'Keefy and Ahrens [27], Croft [28] and Prinn and Fegley [29], I estimate that a 25 km s^{-1} comet with a mass of ca. 1.3×10^{16} kg and a diameter of about 29.2 km (Fig. 3a) could readily generate 1.3×10^{16} kg of superheated H_2O vapor, impacting into a (ca. 4 km) deep ocean. (I assume that the bulk of the comet is composed of ice-H_2O, having a density of about 1000 kg m^{-3}). Evidently, this value is a rather conservative assumption since the impacted oceanic H_2O could also supply an amount of superheated steam to the cometary plume [13,14,15,27,30,31,32]. (A cometary impact on land, of course, would provide lower amount of impacted H_2O vapor. In addition, during cratering process oceanic H_2O immediately penetrating into the initial crater could be also rapidly converted into a superheated steam because the temperature in the center of the crater cavity may reach temperatures of several thousands of degrees [13,14,31]. I also ignore the possible contribution of H_2O (derived from the impacted hydrous minerals) in the ocean floor rocks [33]. This is reasonable since the amount of H_2O vapor provided by the target rock for a cometary impact into the ocean is not more than about of the total amount of the impact-related H_2O [34].
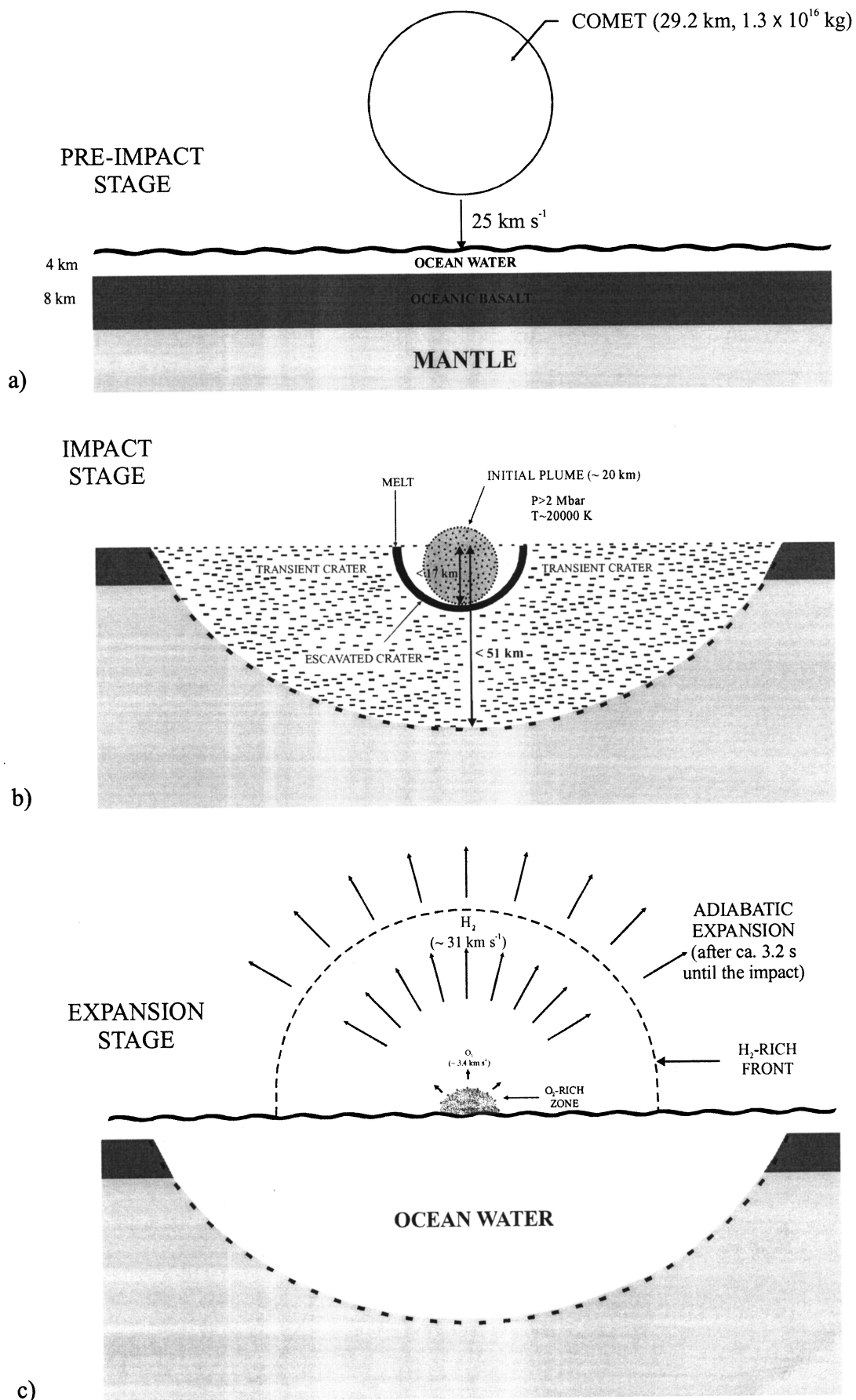
Fig. 3. Cometary impact into ocean. a) The pre-impact stage: the conditions before impact of a 25 km s⁻¹ comet 29.2 km in diameter which strikes a 4 km deep ocean; b) The impact stage: an initial ca. 20 km (spherical) plume with a average temperature ~ 20,000 K and a mean pressure >2 Mbar; a transient <170 km crater with a depth of <51 km; and, c) The expansion stage (after ca. 3.2 s): the H_2-rich front ca. 99 km away from the impact site; the O_2-rich zone of the plume approximately 88 km behind.

The estimated diameter (D_t) of a transient crater formed by a comet at the ocean (basalt) floor is given by Melosh [35]

$$D_t = 0.81 \, \rho_c^{0.33} \, \rho_t^{-0.33} \, d^{0.79} \, v^{0.44}$$

where ρ_c and ρ_t (=2.7 g cm^{-3}) are the densities of the comet and target, respectively, d is the diameter of the comet: in our case D_t<170 km. From studying previously formed craters, the average ratio of escavated crater depth to diameter is about 1:10 [35]. The above comet would produce, therefore, an escavated crater with a depth of ca. <17 km. As the average thickness of the oceanic crust is about 8.0 km, the crater excavation would penetrate <9 km deep into the upper mantle, Fig. 3b. For simplicity, I assume that the excavated target material is mainly composed from the ocean (floor) basalt since the average chemical compositions of oceanic crust and upper mantle are similar [36]. Using the foregoing data it may be found that the excavated mass of the target basalt is about <6 × 10^{16}kg.

6. The Expanding Plume and H$_2$

I assume that cometary H$_2$O vapor was exposed at the moment of impact to a mean temperature of ca. 20,000 K and a mean pressure of ca. >2 Mbar, Fig. 3b. These two values are obtained from the Tillotson equation-of-state, adopting a constant specific heat capacity of ice-H$_2$O: 4 kJ kg^{-1} K^{-1}. (Specific heat capacity of the basalt is ca. 3.6 kJ kg^{-1} K^{-1}). Thermochemical calculations show that at lower temperatures (<20,000 K) and lower pressures (<1 kbar) immediately after the impact shock the cometary portion of the plume would contain mostly O$_2$ and H$_2$. (Molecular dissociation requires ca.15 MJ kg^{-1} for O$_2$ and 218 MJ kg^{-1} for H$_2$). H$_2$ and O$_2$ in the expanding cometary plume may be expected to move out radially away from the impact site, rapidly escaping (or "blowing-off") when the mean kinetic energy per molecule exceeds gravitational potential energy [37].

The above calculations also indicate that the possible formation of O$_2$ within the expanding plume at lower post-shock temperatures (<10,000 K) is significantly affected by the abundances of H$_2$. These calculations over a wide range of assumed plume compositions show that the speciation in a low temperature O-H plume depends on the bulk H/O ratio. In a low-temperature H$_2$-enriched plume, H$_2$O vapor would be the major gaseous component and in a low-temperature H$_2$-depleted plume, O$_2$ would be the major species. Thus, a high H/O ratio would suppress the formation of O$_2$ within the expanding plume and a low H/O ratio would favor this process. For this reason, of crucial importance for generation of O$_2$ is the separation of O$_2$ and H$_2$ within the plume. This would keep them from re-reacting with each other, making ultimately H$_2$O vapor again. H$_2$ could be separated from O$_2$ by either the escape into interplanetary space or chemical reactions with some of the plume constituents. The remainder of the paper is focused on the removal of H$_2$ from the plume by the escape process.

7. The Plume Expansion and the H$_2$ Escape

Here I model the plume generated by an impacting comet as a gas cloud expanding into a vacuum which commences its expansion in uniform thermodynamic state. (For a discussion of the physics of such a model the reader is referred to Melosh [14,35], Vickery and Melosh [38], Zel'dovich and Razier [39] and Zahnle [40]). For simplicity, I assume that the comet and an equal mass of the target are vaporized/shocked and constitute the cometary plume. (This assumption rests on the planar or vertical impact approximation when both the impactor and the target are the same or similar material). Indeed, numerical calculations show that half of the comet kinetic energy is partioned into the target and half remains in the comet, even when the impactor and target are ice-H$_2$O and oceanic basalt, respectively. I also suppose that the mass of

superheated H_2O vapor within the initial plume is simply equal to the mass of the impacting comet.

The initial specific energy available for the expansion of the plume is given by ½(KE – D), where KE (= ½ v^2) is the specific kinetic energy of the comet with a speed v and D is disintegration energy of ice-H_2O. (Complete vaporization for ice occurs at a shock pressure of <1 Mbar. The disintegration of H_2O into O_2 and H_2 requires about 16 MJ kg^{-1}; the vaporization energy for silicates (ocean basalt) is about 13 MJ kg^{-1}). If KE >> D then the energy deposited as heat within the comet is sufficient to vaporize/decompose, at least, the cometary ice-H_2O (into O_2 and H_2) and to vaporize the ocean basalt. H_2 and O_2 would be strongly compressed by the impact shock and then ejected from the expanding transient crater upon decompression, Fig. 3c. Simple thermodynamics then shows that for a m kg and v km s^{-1} comet impacting into a deep ocean the mean (mass-averaged) bulk expansion velocity v_p of the plume is equal <1/2v. (For the present case v_P <12.5 km s^{-1}).

In my model two limiting processes other then the separation of O_2/H_2 within the plume must be considered, however. First, the energy carried out by escaping H_2 must be ≤1/3 KE. Elementary physics then shows that v must be $\geq(2/3)^{1/2}$ v_{esc}, where v_{esc} (=11.2 km s^{-1}) is the escape velocity from Earth, i. e., v ≥9.1 km s^{-1}. Following the same reasoning one finds that most of O_2 would retain within the Earth's atmosphere if the comet speed is ca. ≤37 km s^{-1}. Then a more severe constraint is imposed by consideration of the effect of the comet velocity on the energy required for a decomposition of the plume H_2O vapor. In the absence of additional sources of heat, KE should be much higher than 2D. I shall take KE ≥10 D (ca. ≥160 MJ kg^{-1}) as a very rough estimate of the energy-limited decomposition of the plume H_2O. Simple algebra then shows that that complete thermal decomposition of the plume H_2O vapor requires a comet with, at least, a speed of ca.18 km^{-1} s^{-1}. I suggest, therefore, that if the comet velocity 18 km s^{-1}≤ v ≤37 km s^{-1}, the plume H_2O would be decomposed into O_2 and H_2, and most of its H_2 would escape the Earth.

In the present model, H_2 (ejected in the initial stage of the plume expansion) would concentrate predominantly in the outer (and much faster) front of the rapidly expanding plume separated from the inner part, containing O_2 and the vaporized oceanic basalt (mainly as SiO_2 and MgO) [38], Fig. 3c. Simple thermodynamics shows that the mean (mass-averaged) bulk velocities of H_2 and O_2 within the plume are approximately given by:

$$v (H_2) = (3/2)^{1/2} v \text{ and } v (O_2) = (3/32)^{1/2} v$$

For the cometary impact in question, it can be taken that v (H_2) ~ 31 km s^{-1} and v (O_2) ~ 3.4 km s^{-1}, Fig. 3c.

Average temperature T in the H_2-depleted plume during the (isenotropic) expansion can be roughly calculated as

$$T/T_0 \sim (\rho/\rho_0)^{(\gamma-1)}$$

where T_0 and ρ_0 are the initial temperature (ca. 20,000 K) and density of the initial plume; and, γ (~1.2 – 1.7) is the specific heat ratio [39]. For the present impact the temperature evolution of the H_2-depleted plume is presented in Fig. 4. I assume that the initial density ρ_0 of the plume induced by the current impact is approximately 6 times larger than the density of the comet. I also assume that γ = 1.2 [14]. I hypothesize that this plume becomes hemispherical when its radius greatly exceeds (about 3 times) the radius of the initial plume (ca. 10 km, Fig. 3b). The pressure of the H_2-depleted plume can then be determined adopting ideal gas laws and adiabatic expansion, (Fig. 5).
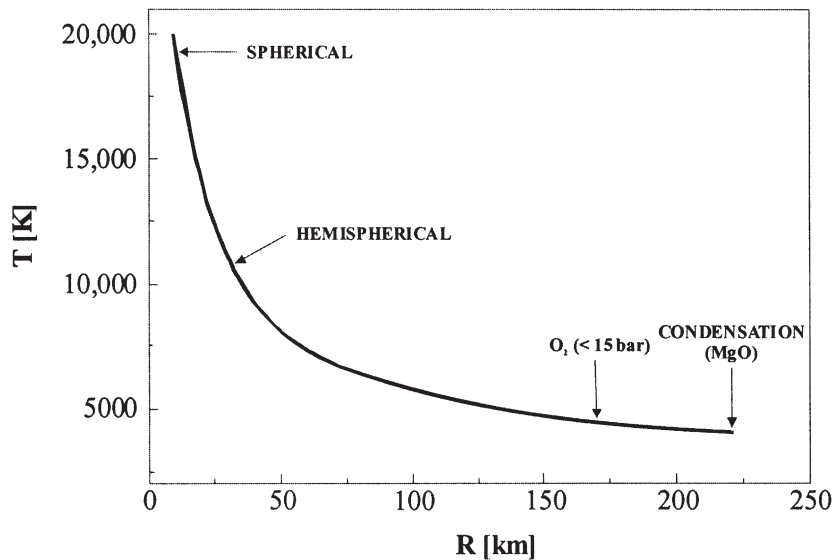
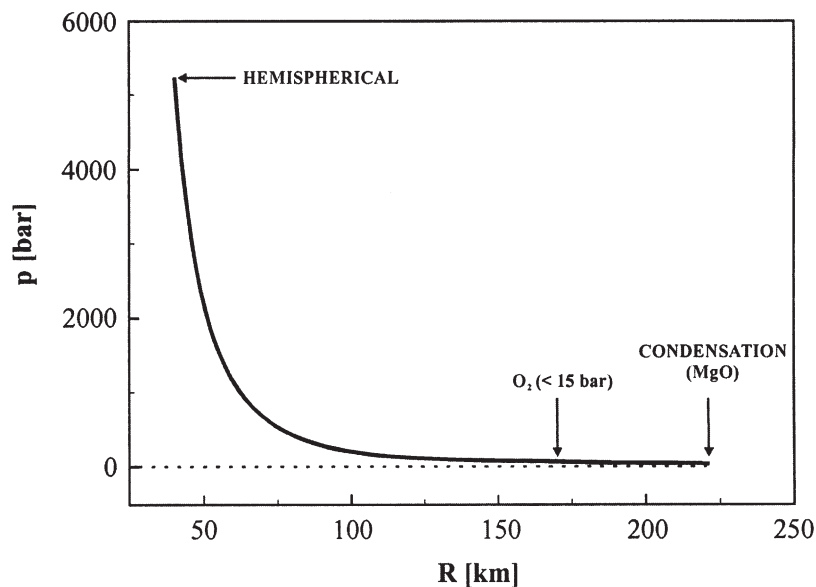Fig. 4. Average temperature vs. radius of the H_2-depleted plume.

Fig. 5. Mean pressure vs. radius of the hemispherical H_2-depleted plume
(after ≥ 3.2 s of the expansion).

For about 13.5 s the expanding (hemispherical) H_2-depleted plume would reach the average temperature of about 4200 K with the mean partial pressure of O_2 of ca. <15 bar, Figs. 4 and 5. After ca. 18 s this plume would expand to about 220 km, adiabatic cooling (to ca. ≤ 3600 K) would condense much of the vaporized MgO, Figs. 4 and 5. (SiO_2 condenses at ca. 2800 K). For about 33 s the H_2-rich front of the plume would be ca. 1000 km away from the impact site, reaching the exobase of the Archean atmosphere. At this point, the O_2-rich zone would be ca. 910 km behind it. For ca. >150 s the O_2-rich plume would further expand and cool-down (to ambient temperature) and cover the entire planet until the plume collapse goes to completion.

Assuming a 100 % impact efficiency, a m kg cometary (or any icy) object impacting into a deep ocean of the pre-oxygenic Earth would therefore generate approximately m kg of O_2 if its speed is within the critical limits of 18 km s^{-1} and 37 km s^{-1}. Short-period comets with periods >20 years have impact velocities 15-35 km s^{-1}, for a mean of ca. 23 km s^{-1} [41]. Some 25 % of these comets collide with Earth with velocities ≤ 18 km s^{-1}, and another 50 % occur with velocities between 18 km s^{-1} and 23 km s^{-1}. [16]. In the present case of cometary impact, the cometary H_2O vapor would create an atmosphere with ca. 1.3×10^{16} kg (0.01 PAL) of O_2. (It is

reasonable to expect that a similar impact on land would provide an equal amount of O_2). Note that 0.01 PAL is "the Pasteur point" or "the first critical level of O_2" (Berkner and Marshall [42] and references therein). In addition, when the O_2 level advances to about 0.1 PAL a powerful O_3 screen starts to form in the upper atmospheric layers. The presence of atmospheric O_3 is essential to the existence of most plant/animal biota since O_3 is the only important absorber of solar near-UV radiation between 2000 and 3000Å.

I did not consider in this report an oxidation reaction of FeO (derived from the vaporized oceanic basalt and the upper mantle) as a loss mechanism of O_2 in the plume. (Oceanic basalt and the upper mantle contain on the average about 9% of FeO) [36]. Simple chemistry indicates that complete oxidation of the basalt-derived-FeO ($4FeO + O_2 \rightarrow 2Fe_2O_3$) in the plume requires only about <5% of the plume O_2. In other words, loss of the O_2 within the plume through oxidation of the basaltic FeO would be minor.

Another omission of my model is the absence of a pre-oxygenic Earth's atmosphere. Direct evidence of a reducing atmosphere has been claimed in the past, but this evidence is no longer regarded as conclusive. There is a growing consensus, however, that in the Archean period for which data is available, the atmosphere was neutral, with negligible amounts of free O_2. It is considered likely that the atmosphere at this time was composed of N_2 (ca. 0.8 bar), CO_2 (ca. 0.2 bar), CO and H_2O [1]. Obviously, the chemistry inside the expansion plume would be rather complex, caused by mixing and interacting of the plume gaseous components with the surrounding atmospheric gases. Clearly, chemical reactions between N_2 and O_2 would dominate within the plume. Preliminary thermochemical calculations, however, indicate that under the assumed conditions only approximately <1% of the plume O_2 could be consumed through these reactions. (Any detailed high temperature chemistry within a cometary plume is deferred to a later paper).

Free O_2 generated by the current impact could be partly consumed by oxidation of upwelling ocean waters containing Fe^{2+} and reduced metamorphic and volcanic gases mainly H_2, CO, SO_2 [43]. If upwelling oceanic Fe^{2+} ions were about 3 ppm and a mean oceanic upwelling rate of ca. 5 m y^{-1}, then the oceanic Fe^{2+} sink rate for free O_2 was about 10^{10} kg y^{-1}, neglecting all other losses [44]. After 10^6 y, therefore, approximately all cometary O_2 (ca. 1.3×10^{16} kg) would be consumed by the oceanic sink.

8. The Cometary Impact Rate and Implications

The Earth has been impacted by comets and asteroids throughout its geologic history. Terrestrial collisions with a comet >10 km in diameter have been estimated as about 1 per 10^8 y [9], but occasional cometary showers could occur at intervals of tens of millions years [45]. The impact rate appears to have been relatively constant back to about 3.8 Ga when it began to rise. At times earlier than about 3.8 Ga, there appears to have been an exponential increase in the rate. In the pre-oxygenic Earth's history, the high cometary impact flux was probably a significant factor in the modification of the atmosphere, hydrosphere and biosphere.

Kring and Cohen [46] estimate that during the impact cataclysm [ca. 3.9 Ga] the Earth's surface was aggravated by tens of thousands (over 22,000) of impact events, producing (at an average rate of once per 20 y) craters with diameters ≥20 km. Coincidently, the earliest isotopic evidence of life on Earth is also ca. 3.9 Ga [47]. According to Kring and Cohen [46] the impact cataclysm affected the early evolution of life, by causing devastation at the Earth's surface, producing suitable conditions for primitive anaerobic (bacterial) life in subsurface environments.

Chyba, *et al.* [16] have examined cometary H_2O influx, using the latest estimates of comet/asteroid fluxes during the period (Hadean/Archean) between 4.4 Ga and 3.8 Ga, when bombardment of the inner Solar System was thought to be especially severe. According to these authors, the comet influx on the pre-oxygenic Earth could be 10^4-10^5 times greater than currently observed. This would translate into a rate 10^4-10^3 y for the comet bigger than the comet Haley (equivalent in volume to a sphere about 10 km in diameter). (Chyba, *et. al.* [16] computed that

the Earth would have gained more than 0.2-0.7 of the terrestrial ocean mass (ca. 1.4×10^{21} kg is the present mass of the oceans) in that billion-year period). Adopting these values, one finds that between 0.3 and 1×10^{19} kg of free O_2 could be generated during the heavy bombardment period (ca. 4.4 to ca. 3.8 Ga) by the impact-induced thermal decomposition of cometary H_2O, if only ca. 1 % of the comets had the velocities between 18 km s^{-1} and 37 km s^{-1}. Any such enormous flux of free O_2 into the atmosphere of the early Earth would have to be largely lost, possible mechanisms include atmospheric erosion by highly energetic comets and asteroids hydrodynamic escape, the effect of a strong primitive solar wind, oxidation of the oceanic Fe^{2+}, reduced minerals and volcanic gases, photochemical dissociation and incorporation into the Earth's core. Obviously, the physics and chemistry of these processes are complex, and a more detailed study would be require to examine them properly.

9. Long Period Comets, O_2 and Ar

In general, long period comets are the most common ones: at least 80% of all comets have long periods have impact velocitities between 40 km s^{-1} and 70 km s^{-1} (and a mean ca. 55 km s^{-1}) [41,48,49]. (Hale-Bopp, LINEAR and McNaught-Hartley comets are the examples of long period comets). Stern *et al.* [50] reported the spectroscopic detection of Ar in comet Hale-Bopp. They found that the ratio of ^{36}Ar to O (presumably from H_2O) is about 2.5×10^{-3}. The ratio of ^{36}Ar in the Earth's atmosphere to O_2 is ca. 1.8×10^{-4}. Compared to the Hale-Bopp ratio, the ^{36}Ar abundance is depleted in LINEAR by a factor of 10; for McNaught-Hartley the enrichment factor is about 2 [51]. Hence, if a LINEAR-type comet (with 70 % H_2O) generated all O_2 in the present atmosphere, it would supply the entire ^{36}Ar budget in this atmosphere. It seems, therefore, reasonable to hypothesize that long period comets could be responsible for a significant fraction of present-day atmospheric ^{36}Ar. This does not mean, however, that atmospheric O_2 of today is of cometary origin. Indeed, in weakly reducing milieu of the Archean cometary O_2 would be mainly lost through various oxidation processes, whereas chemically inert Ar would be retained in the Earth's atmosphere. In addition, the rate of photosynthetic production of O_2 is extremely high, and it is estimated that at present time all O_2 (ca. 1.2×10^{18} kg) in the atmosphere passes through the photosynthetic cycle in 2000 y [52].

If long period comets had brought in Ar (and other noble gases) that was later lost, the process had to occur in the first 100 Ma of Earth geologic history [53]. Furthermore, approximately 40 impact basins with a diameter of ca. 1000 km and several with diameters about 5000 km were produced on the Earth during the impact cataclysm. All these impactors were large enough to disrupt the primitive atmosphere and the largest bolides would remove a big part (including cometary O_2 and Ar) of it. I can conclude, therefore, that if cometary impact event(s) produced atmospheric O_2 and Ar it had to occur after the impact cataclysm.

10. Cometary Impacts and Early Oxygenic Photosynthesis

Certainly, an abrupt rise of O_2 to ca. 10^{-4} PAL triggered by a cometary impact would cause a crisis for the primitive anaerobic microbial life on the pre-oxygenic Earth during the Archean (ca. 3.8 Ga to 2.2 Ga). Indeed, these life forms would be actually poisoned by such an excess of O_2 in their living environment, triggering wholesale extinctions. I wish briefly to speculate about a possible way of generating this level of O_2 on the pre-oxygenic Earth that would be compatible with my scenario. It consists of ca. 7 km diameter comet (or few of its tightly clustered fragments) with a speed (18 km s^{-1} $\leq v \leq$ 37 km s^{-1}) impacting into a deep ocean (or on land). Alternatively, multiple cometary impacts (within a short period of time) or a "shower" of small (<1 km) comets with the corresponding bulk velocity and mass would also be capable to create the same level of O_2. Indeed, such impacts would be more efficient in generating superheated H_2O vapor (i. e., free O_2) than a single large impact for the same bulk mass of the cometary

material [28]. However, once the atmosphere had become oxygenic, H_2 escape to interplanetary space would cease and impacting small comets would deliver only H_2O to the Earth's ocean.

According to Shoemaker, *et al.* [9], the collisions with a ≥5 km comet during Archean may have been much higher than that currently observed (about 1 per 10^6 y). It appears likely, therefore, that between the early Archean (ca. 3.8 Ga ago) and prior to the early Proterozoic (ca. 2.2 Ga ago), Earth was struck, at least, 100 times by comets larger than 5 km which are in the approximate size range necessary to generate 10^{-4} PAL of free O_2, provided they have velocities within the proper range (18 km s^{-1} ≤ v ≤ 37 km s^{-1}). These impacts may cause periodic formation of (transient) oxygenic atmosphere and ocean, implying that the impact-induced generation of free O_2 on pre-oxygenic Earth may have occurred more then once, at least, before Proterozoic. Thus, the cometary impacts are consistent with the periodic destruction of the early anoxygenic atmosphere and formation of early transient oxygenic atmosphere and ocean. This implies that primitive anaerobic microbial life, if it evolved in the early ocean, was globally extinguished more than once. On the other hand, this O_2 crisis would create a suitable environment for a new but more advanced aerobic (photosynthetic) life-form which would permit a build up of O_2 to the present-day level.

Assuming that the impact-related H_2O vapor (decomposed through the thermal process) is completely converted into O_2 and H_2, simple arithmetic reveals that 1.4×10^{14} kg (i. e. 100 ppb of total ocean H_2O) of this vapor would generate an atmosphere with 10^{-4} PAL of free O_2. Thus, it appears that the hypothesis of an early (oxygenic) atmosphere requires an entirely small amount of thermally decomposed H_2O vapor.

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