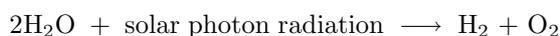


**ASTRONOMICAL RADIATION SOURCES AND THE
ORIGIN OF ATMOSPHERIC OXYGEN OF
PRE-OXYGENATED EARTH: SOLAR PHOTON RADIATION**

P. I. PREMOVIĆ

*Laboratory for Geochemistry, Cosmochemistry and Astrochemistry, University of Niš,
P.O. Box 224, 18000 Niš, Serbia
E-mail: pavle.premovic@yahoo.com*

Abstract. In this preliminary report, I explore a possibility that the solar photon radiation source is related to the origin of free oxygen (O₂) derived from oceanic and/or atmospheric water on pre-oxygenated Earth which has been overlooked in the previous studies. The pre-oxygenated Earth was probably subject to intense solar photon radiation (ultraviolet light, X-rays and gamma rays), greatly increasing during short times of solar flares and superflares. Overall effect of this radiation on the oceanic and atmospheric water on pre-oxygenated Earth is shown in the following reaction



I tentatively suggest that the solar photon radiation and subsequent geochemical processes may have contributed to the origin of O₂ in the atmosphere on pre-oxygenated Earth.

1. PRE-OXYGENATED EARTH

The age of solar system has been determined to be approximately 4.6 Ga from numerous geochemical data. The first era (about 4.6 Ga to 2.5 Ga ago) in the geological history of Earth is Precambrian, Fig. 1. The first eon are the Hadean (about 4.6 Ga to 3.8 Ga ago). The Hadean eon is followed by the beginning of Archean time about 3.8 Ga ago, an Eon that lasted until about 2.5 Ga ago, when the Proterozoic Eon was initiated.

From studies on the oldest known terrestrial minerals, zircons (ZrSiO₄) from Australia, the presence of oceans on the Earth has been inferred as early as 4.4–4.0 Ga ago (Valley et al. 2002, and references therein).

The atmosphere in the first 100 Ma of the Hadean came from outgassing (release of gases from the solid Earth) and impact degassing (release of gases when comets and the ice H₂O-rich asteroids impacted). Volcanoes give out mostly H₂O and CO₂, with relatively small quantities of H₂, CO, and CH₄, and no O₂.

A major, near catastrophic event, seems to have occurred in the first 50 million years after the initial Earth had formed. A body roughly the size of Mars, i.e., another terrestrial-type planet or a huge asteroid, collided violently with the Earth.

The impact-related material in orbit formed the Moon. The kinetic energy of the Mars-sized body impacting the primitive Earth must have been very great, so great that it would have provided enough energy probably to strip away the original Hadean atmosphere.

Another major event in the Hadean years was what is known as the "Late Heavy Bombardment", in which a notable fraction of larger objects near the Earth were involved in frequent impacts onto the planet and its Moon. For this reason, in this paper I will focus my attention on the Archean thus after the Late Heavy Bombardment. For convenience, I shall refer to the Archean Earth (before the Proterozoic: 2.4 to 0.54 Ga ago, Fig. 1) as pre-oxygenated Earth.

Several lines of geological and geochemical evidence indicate that the the atmosphere throughout the pre-oxygenated time (3.8 - 2.5 Ga ago) were probably weekly reducing CO₂-N₂ with small amounts of H₂. The mass of O₂ in the present-day atmosphere is estimated to be 1.2×10^{21} g. The fact that oxygen is present in considerable quantity (ca. 1.2×10^{24} g) bound in the oceanic/terrestrial H₂O of today is evidence that much of the atmospheric O₂ may be derived from these sources. Indeed, current production rate of O₂ in photosynthesis is extremely high (10^{10} g s⁻¹), and it is estimated that at present time all O₂ in the atmosphere passes through photosynthetic cycle in 2000 years.

In the atmosphere on pre-oxygenated Earth the maximum partial pressure of oxygen was probably about 5×10^{-8} atm or about 10^{-7} the present atmospheric level (PAL) (Haqq-Misra et al. 2011). At about 2.4 to 2.2 Ga ago during the so-called Great Oxidation Event atmospheric O₂ risen above up to about 3×10^{-2} atm. It is generally considered that this oxygenation of the atmosphere was caused mainly by biological processes such as the production of O₂ through photosynthesis by marine microorganisms called cyanobacteria.

2. CURRENT HYPOTHESES

Currently, there are two (major) scientific hypotheses about the origin of free O₂ on pre-oxygenated Earth. The first hypothesis, free O₂ was generated through photosynthetic activity of anoxic microorganisms; second hypothesis, free O₂ was produced by the direct solar photodissociation of atmospheric water (H₂O). This process is considered to be only capable of yielding small amounts of free O₂ (Kasting, 1993, and the references therein). Recently, Premović (2003) proposed a third, rather controversial, hypothetical alternative, 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 pre-oxygenated atmosphere. These hypotheses still remain (more or less) speculative and warrant further research.

The purpose of the present review is to explore a possibility that dissociation of oceanic H₂O and/or atmospheric H₂O vapor by the solar photon radiation can generate O₂ in the atmosphere on pre-oxygenated Earth.

3. SOLAR IONIZING RADIATION

The Sun has been probably the single greatest source of astronomical radiation to pre-oxygenated Earth on a continuing basis. This ancient Earth was probably subject to intense solar ionizing radiation greatly increasing during short times of solar winds,

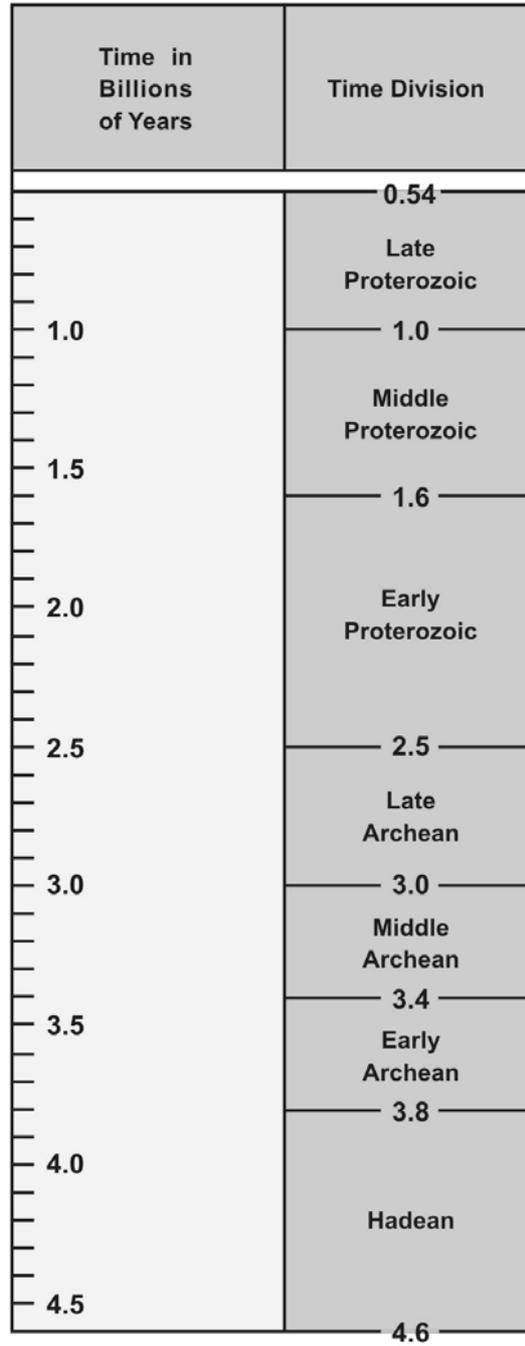
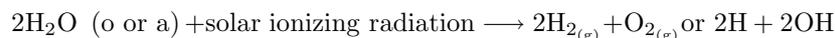


Figure 1: The divisions of Precambrian time.

flares and superflares. There are two types of solar ionizing radiation. The first one is electromagnetic radiation mainly composed of the energetic UV, X- and gamma (γ)-ray photons; the other main type, so-called solar cosmic rays (SCR), consists predominantly of high energy protons and electrons (95 %), alpha particles (4 %) and isotopes of helium (He) and neon (Ne). X- and γ -rays and cosmic rays may also originate from non-solar sources often as galactic cosmic radiation coming from outside the solar system.

Overall effect of the above two types of solar ionizing radiation on oceanic H₂O (o) or atmospheric H₂O vapor (a) on pre-oxygenated Earth is shown in the following direct dissociation reaction



where g stays for gas phase. This dissociation is followed by escape of H and H₂ in space. In general, the loss of hydrogen to space should be approximately equal the total O₂ content in the pre-oxygenated atmosphere. Probably, similar reaction can be written for the atmospheric CO₂ [$2\text{CO}_{2(g)} + \text{solar ionizing radiation} \longrightarrow 2\text{CO}_{(g)} + \text{O}_{2(g)}$] but in this report my attention will be focused only oceanic H₂O.

The amount of H₂O decomposed by this reaction depends strongly on the timescale of radiation emission and the fraction of the incident radiation that can reach a given level of atmosphere. Under the conditions of the current atmosphere, the photolysis rate of atmospheric H₂O vapor corresponds to about $5 \times 10^5 \text{ g s}^{-1}$. The O₂ content in the contemporary atmosphere exceeds approximately 200-fold its content in the oceanic water. This implies that almost the entire volume of O₂ generated by the solar ionizing radiation of oceanic H₂O would probably go to the pre-oxygenated atmosphere.

4. SOME ROUGH CALCULATIONS

Before any further discussion, let us do some rough (but informative) calculations. The present atmospheric level of oxygen is about 21 % which has mass of 1.2×10^{21} g. (Ancient O₂ concentrations are generally expressed as fractions of PAL of O₂). If about m kg of atmospheric H₂O is converted directly into O₂ it would generate approximately m kg of O₂. A simple calculation shows that 2.5×10^{14} g of H₂O is necessary to convert by any solar ionizing radiation (or any of their combination) to generate the pre-oxygenated atmosphere with 5×10^{-8} atm of O₂. Assuming that the mass in the global ocean on pre-oxygenated Earth was about the same as today (1.4×10^{24} g), it means that only an extremely small fraction (about 0.2 ppb) of their H₂O was necessary to convert into O₂. This requires to decompose about 3×10^{18} H₂O molecules per cm^{-2} of the global ocean and is equivalent to about 0.7 μm of the global ocean. If during pre-oxygenated Earth there was as much H₂O vapor in the atmosphere as we assumed to be present today 1.5×10^{18} g then 170 ppm of this water was necessary to convert into O₂. During the Great Oxidation Event the atmosphere contained about 3×10^{-2} atm O₂ or 1.5×10^{20} g. Thus, photochemical dissociation of 100 times the amount of atmospheric H₂O vapor could produce all the O₂ at that time.

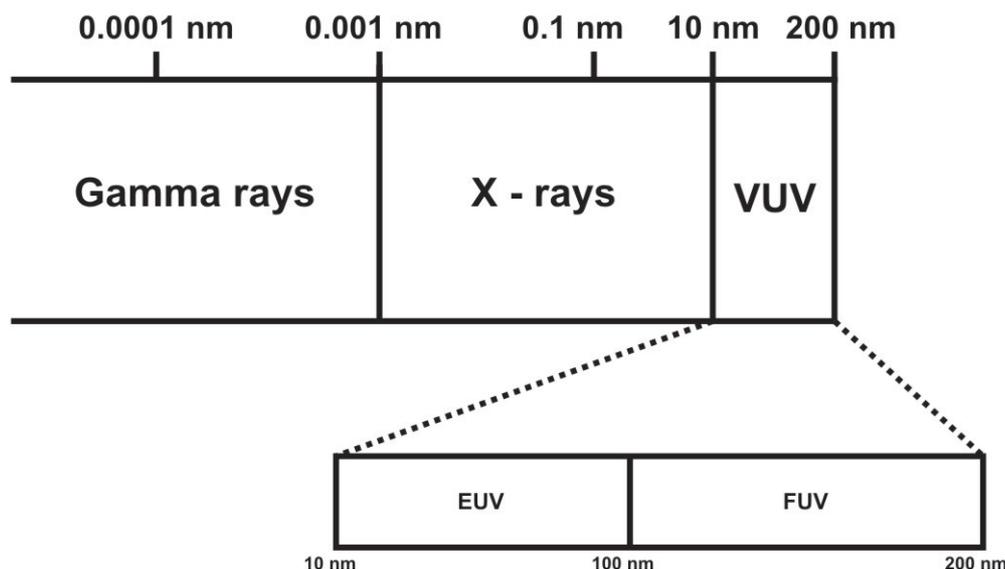


Figure 2: The spectrum of the VUV-X radiation and γ -rays.

5. SOLAR PHOTON RADIATION

As I stated above this review addresses only dissociation of oceanic and atmospheric H_2O by solar photon radiation, leaving consideration of solar winds, SCR and galactic cosmic radiation for future work. The direct photodissociation of H_2O molecules requires solar photons of wavelengths less than about 200 nm. These are photons of the following radiations: (a) the vacuum ultraviolet light (200-10 nm), (b) X-rays (ca. $10 - 10^{-3}$ nm) or (c) γ -rays (ca. $< 10^{-3}$ nm), Fig. 2. The vacuum ultraviolet (VUV) radiation is divided into the following two regions: the far ultraviolet (FUV) (ca. 100-200 nm) and the extreme ultraviolet (EUV) (ca. 10-100 nm). The present-day (upper) atmosphere absorbs almost all photons of solar VUV, X-rays and γ -rays. The main molecular absorbers of these photons are ozone (O_3), nitrogen (N_2) and O_2 . The quantity of solar VUV-X radiation received at Earth's surface or at any atmospheric level depends on two main variables: the emission of radiation by the Sun and its extinction through absorption and scattering by the constituents of atmosphere.

6. MODEL ATMOSPHERE 1.

Models of the pre-oxygenated atmosphere are diverse as the, often, contradictory, evidence on which they are based. In the study of atmospheric composition it is often convenient to use simplified photochemical atmospheric models. Such models have proved very useful in studies of certain aspects of the atmospheric chemistry. I assume for simplicity with a model of the pre-oxygenated atmosphere which is thick enough to prevent complete evaporation of global ocean and with enough ambient heating to prevent complete freezing of this ocean. I will begin with the simplest pos-

sible model of this atmosphere which contains only H₂O vapor and it is saturated with it at about 25 °C. I assume that an atmospheric column density is about 30 g cm⁻² for H₂O vapor or about 10²⁴ molecules cm⁻². Of note, the column densities of H₂O vapor in the existing atmosphere are about 2.5 g cm⁻². I will name this atmosphere model as MA1 (a short notation for model atmosphere 1). In fact, MA1 is the excellent starting point for my future investigation since it is so thin that the all incident ionizing radiation reach the ocean surface. My model represents a simplification of the real pre-oxygenated atmosphere and, of course, the validity of my conclusions will therefore depend upon the assumptions I made.

7. VUV-X AND γ -RAY PHOTONS

Astronomical consideration indicates that the overall luminosity of the Sun during the pre-oxygenated period was approximately 70-75 % of the present day luminosity. In contrast, the VUV, X- and γ -ray luminosity during this time was likely much higher than today. Therefore, much higher fluxes of solar photons of VUV-X radiation and γ -rays were reached the pre-oxygenated Earth than at present. Table 1 provides rough estimates of solar photon fluxes of VUV, X-rays and γ -rays reaching the ocean surface of pre-oxygenated Earth with MA1. However, the present-day solar photon flux of γ -rays compared to that of VUV-X radiation is lesser by at least for five orders of magnitude (Rutten and Cram, 1981) and thus they were probably far less important in the direct solar photodissociation of pre-oxygenated oceanic and atmospheric H₂O. Thus, I here limit my discussion to dissociation of oceanic and atmospheric H₂O by solar VUV-X photons.

According to Table 1, a mean total photon flux of solar VUV-X reaching this surface is probably about 1.5×10^{11} photons cm⁻² s⁻¹ with a mean total energy flux of roughly about 7 ergs cm⁻² s⁻¹ (or 4.5 TeV cm⁻² s⁻¹). A given photochemical process is generally characterized by the quantum efficiency (QY) which is determined as a ratio between the number of reacted molecules or the molecules of the reaction product and the number of the absorbed photons. The QY (H₂O) for liquid H₂O dissociation under the VUV-X radiation is higher than 1 (Heit et al., 1998). This gives a minimum photodissociation rate of ca. 1.5×10^7 g s⁻¹ of H₂O in the global ocean.

If we make the reasonable assumption that a mean total H₂O photodissociation rate for MA1 is about 2×10^{11} molecules cm⁻²s⁻¹, as estimated for the pre-oxygenated atmosphere by Brinkmann (1969), then this process would decompose 3×10^7 g s⁻¹ of H₂O in MA1.

A major O₂ sink on pre-oxygenated Earth was volcanic gases (primarily H₂). Kump et al. (2001) estimated that these gases currently consumed ca. 5×10^5 g s⁻¹ O₂ and suggested that during photosynthetic Earth this consumption was somewhat higher. On the pre-oxygenated Earth with MA1 the photolysis of oceanic and atmospheric H₂O probably generate roughly this amount of O₂. If this is correct than QY (O₂) for this photolysis is about 1.7×10^{-2} and it is probably an upper limit.

8. SOLAR FLARES AND SUPERFLARES

Solar flares are magnetically driven explosions on the surface of the Sun which creates an energetic burst of electromagnetic radiation mainly in the form of VUV-X and γ

Table 1: Rough estimates of average photon fluxes on the surface of the pre-oxygenated Earth with MA1 (see the text). These fluxes are calculated assuming that solar activity was moderate (so-called the quiet Sun).

Wavelength [nm]	Photon flux [10^{10} photons $\text{cm}^{-2}\text{s}^{-1}$]
92-120	6.0
36-92	4.5
10-36	4.5
2-10	0.3
0.1-2	0.2
<0.01	10^{-6}

Table based on the solar data of Ribas et al. (2005).

radiation which reaches the Earth. The most of these flares have energy of 10^{32} erg which is about 10^3 times more than that of the quiet Sun but they only last for about 10^3 s. In the pre-oxygenated Earth's time the Sun would have had on average 5 such flares per day. These flares would photochemically generated at least 3×10^7 g s^{-1} of O_2 (averaged over a year) in MA1.

Recently, Schaefer et al. (1999) discovered stellar flares with 10^2 to 10^7 times more energy than the largest solar flare. These superflares have durations of hours to days. According to Rubenstein and Schaefer (2000) the Sun has not had any superflares $> 10^{36}$ erg in the last 10^9 years or so. Of course, this does not mean that no solar superflares were during the pre-oxygenated Earth. Let us assume that the superflare did occur with 10^{36} erg once during the pre-oxygenated era and lasted for about a week. This gives 6×10^9 g s^{-1} of O_2 (averaged over a year). However, the superflares appear to take place every few million years so their generation rate of O_2 in MA1 could be much higher. Thus, I tentatively conclude that volcanic gases on pre-oxygenated Earth could be overwhelmed (at least for a short time) by the photochemically generated O_2 .

In conclusion, I tentatively conjecture that dissociation of oceanic and/or atmospheric H_2O by solar photon radiation could generate the important levels O_2 (at least for a short time) on pre-oxygenated Earth. I realize that this paper is rather speculative. However, I hope that through this initial work and anticipated future work, I will develop of testable hypotheses regarding the relationship (or lack thereof) between the solar ionizing radiation and O_2 on pre-oxygenated Earth.

References

- Haqq-Misra, J., Kasting, J. F. and Lee, S.: 2001, Availability of O_2 and H_2O_2 on pre-photosynthetic Earth. *Astrobiology*, **11**, 293.
- Heit, G., Neuner, A., Saugy, P.-Y. and Braun, A. M.: 1998, Vacuum-UV (172 nm) actinometry. The quantum yield of the photolysis of water. *J. Chem. Phys.*, A **102**, 5551.
- Kasting, J. F.: 1993, Earth's early atmosphere, *Science*, **259**, 920.
- Kump, L. R., Kasting, J. F. and Barley, M. E.: 2001, Rise of atmospheric oxygen and "the upside-down" Archean mantle. *Geochem., Geophys. Geosyst.* G3. 3 paper number 2000GC000114.

- Premović, P. I.: 2003, Cometary Impacts into Ocean: Thermochemical Equilibrium Calculations of High-Temperature O₂ Generation on the Early Earth. *International Journal of Impact Engineering*, **29**, 575.
- Ribas, I., Guinan, E. F., Gudel, M. and Audard, M.: 2005, Evolution of the solar activity over time and effects on planetary atmospheres. I. High-energy irradiances (1-1700 Å). *Astrophys. J.*, **622**, 680.
- Rubenstein, E. P. and Schaefer, B. E.: 2000, On solar analogues caused by extrasolar planets? *Astrophys. J.*, **529**, 1031.
- Rutten, R. J. Cram, L. E.: 1981, Part I: Introduction, in S. D. Jordan (Ed.), The Sun as a Star, CNRS-NASA Monograph Series on Nonthermal Phenomena in Stellar Atmospheres, NASA SP-450, Washington, 3-7.
- Schaefer, B. E., King, J. R. and Deliyannis, C. P.: 2000, *Superflares on ordinary solar type stars. J.*, **529**, 1026.
- Valley, W., Peck, W. H., King, E. M. and Wilde, S. A.: 2002, A cool early Earth. *Geology*, **30**, 351.