

# A POSSIBLE RELATIONSHIP BETWEEN THE GREAT OXIDATION EVENT AND THE PALEOPROTEROZOIC SNOWBALL EARTH EVENT

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## Abstract

Recent progresses of studies on the rise of atmospheric oxygen during 2.4-2.1 billion years ago (the Great Oxidation Event), the Paleoproterozoic snowball Earth event occurred 2.3-2.2 billion years ago, and a possible relationship between them are reviewed and discussed. Formation of manganese ore deposits at 2.2 billion years ago suggests that the rise of oxygen may have occurred just after the Paleoproterozoic snowball Earth event and, also, an overshoot of the atmospheric oxygen level is suggested to have occurred 2.2-2.1 billion years ago. Numerical results with a coupled model of biogeochemical cycle, photochemical reactions, and hydrogen escape to space shows that an extremely hot climate in the aftermath of the snowball Earth events causes unusually high primary productivity in the ocean through intensive chemical weathering, which results in a transition of the atmospheric oxygen levels from low to high stable steady-states, with an extensive and long-lasting overshoot. Thus, the rise of oxygen should have required perturbation to the system which made the oxygen production rate one order of magnitude higher than the normal rate. Such an extremely large perturbation could have been caused only by the snowball Earth event.

**Keywords:** oxygen, Great Oxidation Event, snowball Earth, cyanobacteria

## 1. Introduction

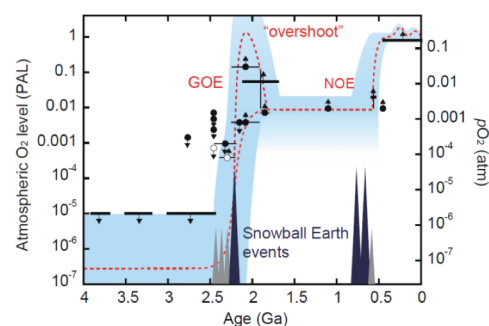
A rise of oxygen (O<sub>2</sub>) in the atmosphere may be one of the most critical factors for the evolution of life during the Earth's history. The concentration of O<sub>2</sub> in the atmosphere is 20.9% at present, while there would have been little O<sub>2</sub> in the atmosphere of early Earth. As shown in Fig. 1, the atmospheric levels of O<sub>2</sub> would have risen from < 10<sup>-5</sup> of the present atmospheric level (PAL) to 10<sup>-2</sup>-10<sup>-3</sup> PAL, sometime between 2.4 and 2.1 billion years ago (Ga) [e.g., 1]. This episode is called the "Great Oxidation Event" or GOE [e.g., 1-3].

Oxygenic photosynthesis due to cyanobacteria would have been responsible for the GOE. Although the age of emergence of cyanobacteria

has been a matter of debate, it should have appeared, at least, before the GOE, probably more than several hundred million years before the GOE [e.g., 4-6].

As seen in the stratigraphy of the Transvaal Supergroup in the Griqualand West region in South Africa, iron and manganese (Mn) bearing units of the Hotazel Formation, the first large-scale sedimentary Mn ore deposits in the Earth's history, have been formed just after the Makganyene snowball Earth event (global glaciation) at ~2.2 Ga (Fig. 2) [7, 8]. Because Mn has a high oxidation potential, which cannot be oxidized virtually without O<sub>2</sub>, it is suggested that this would be an evidence for the rise of O<sub>2</sub> just after the Makganyene snowball Earth event [8].

In this paper, a hypothesis on this issue proposed recently [9] will be reviewed, and a possible relationship between the snowball Earth event and the rises of O<sub>2</sub> will be discussed.



**Fig. 1** The history of O<sub>2</sub> in the atmosphere. The atmospheric O<sub>2</sub> levels would have risen mainly in the two periods: the Great Oxidation Event (GOE) during 2.4-2.1 Ga and the Neoproterozoic Oxidation Event (NOE) during 0.8-0.6 Ga [e.g., 1]. An overshoot of O<sub>2</sub> may have occurred in 2.2-2.1 Ga [e.g., 14-16]. Arrows with filled circles and bars are constraints from geochemical studies.

## 2. Stability of atmospheric oxygen levels

There seems a time gap between the emergence of cyanobacteria which produces O<sub>2</sub> and the rise of

O<sub>2</sub> in the atmosphere (i.e., GOE) as described in the previous section. The levels of the atmospheric O<sub>2</sub> were stable below 10<sup>-5</sup> PAL before the GOE (> 2.4 Ga) [10, 11]. The O<sub>2</sub> levels would have been stable around 10<sup>-2</sup>-10<sup>-3</sup> PAL between the GOE and another oxygen-rise event occurred 0.8-0.6 Ga (called the “Neoproterozoic Oxidation Event” or NOE) [1, 12], and also stable around 1 PAL after the NOE (~during the Phanerozoic) (Fig. 1). Because a residence time of O<sub>2</sub> in the atmosphere is on the order of 10<sup>6</sup> years during the Phanerozoic, the stability of the atmospheric O<sub>2</sub> levels on the order of 10<sup>8</sup> years cannot be explained without some unknown negative feedback mechanisms which stabilize the atmospheric O<sub>2</sub> levels. There seems to be multiple (at least, three) stable levels of the atmospheric O<sub>2</sub>, and the rises of O<sub>2</sub> in the GOE and the NOE could have corresponded to transitions between those stable levels [e.g., 13].

Goldblatt et al. (2006) [13] proposed a model which explains bistability of atmospheric O<sub>2</sub> levels (i.e., a model with two stable O<sub>2</sub> levels); one is low (10<sup>-5</sup> PAL) and the other is high (10<sup>-2</sup> PAL) atmospheric O<sub>2</sub> levels [13]. This is derived from a nonlinear increase in the lifetime of atmospheric O<sub>2</sub> due to production of ozone from O<sub>2</sub> in the atmosphere. The ozone shields troposphere from ultraviolet (UV) flux from the Sun, because UV flux promotes oxidation of CH<sub>4</sub> which consumes O<sub>2</sub> at last, once the O<sub>2</sub> level exceeds 10<sup>-5</sup> PAL [13]. It is however difficult for the atmospheric O<sub>2</sub> levels to make a transition from low to high stable steady-states without unusually large perturbations to a carbon biogeochemical cycle system. Therefore, it could have been possible that the low O<sub>2</sub> levels (<10<sup>-5</sup> PAL) have persisted for several hundred million years after the emergence of oxygenic photosynthesis. The reason for the transition of the atmospheric O<sub>2</sub> levels during the GOE is either by a significant increase in oxygen input from the biosphere or by a decrease in reductant input from Earth's interior [e.g., 13]. However, the actual mechanism to cause the changes has not been clear.

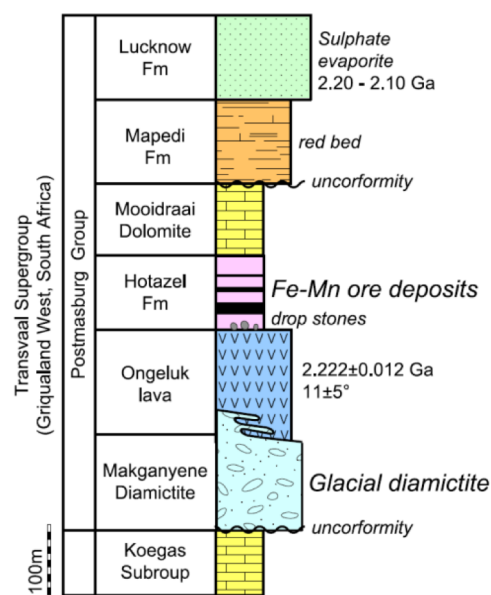
Recent discoveries of geochemical evidence for deep-water oxygenation at 2.1 Ga in the Francevillian Group, the Republic of Gabon [14], and of the global deposition of sulfate minerals at 2.2-2.1 Ga [15, 16] suggest that the O<sub>2</sub> levels may have risen more dynamically with an intensive overshoot, up to ~0.1-1 PAL and lasting for ~10<sup>8</sup> years (Fig. 1) [1, 15]. Such a dynamical behavior should provide strong constraints on a mechanism and magnitude of reduction-oxidization (redox) budget change during the GOE. Also, it is interesting to note that the rise of O<sub>2</sub> seems to have occurred just after a snowball Earth event (global glaciations), as described below. Hence, there might have been causal relationship between them.

### 3. Rise of atmospheric oxygen triggered by snowball Earth event

We proposed a possible mechanism for the rise of O<sub>2</sub> with an intensive overshoot, which would have occurred inevitably as a result of termination of the snowball Earth event [9].

As shown in Fig. 2, a massive deposition of Mn-oxides in the Hotazel Formation occurs just after a deposition of glacial sediments of the Makganyene Diamictite Formation. The glacial diamictite is overlain by volcanic lavas of the Ongeluk Formation from which an age of 2.222 ± 0.013 Ga and a paleolatitude of 11 ± 5° are reported, providing an evidence for low-latitude glaciations, that is, a snowball Earth event [7, 8].

In the snowball (globally ice-covered) climate, the globally- and annually-averaged surface temperature (hereafter, just describes the surface temperature) becomes -40°C, hence all the surface water should freeze completely, which enables volcanic CO<sub>2</sub> to accumulate in the atmosphere until the ice melts [17]. A 0.7 bar of CO<sub>2</sub> is required to accumulate to melt the surface ice at 2.2 Ga when luminosity of the Sun was probably 83% of that at present [18, 19]. After the melting of ice, the surface temperature becomes 60°C because of strong greenhouse effect of 0.7 bar of CO<sub>2</sub> (Fig. 3)

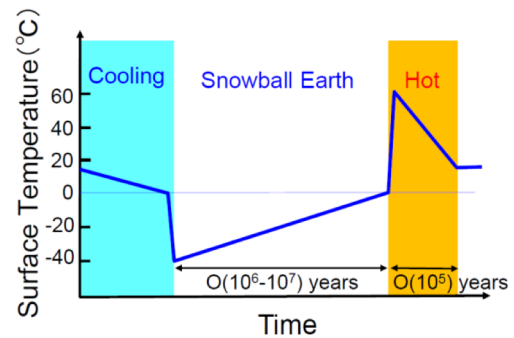


**Fig.2** Stratigraphy of the Transvaal Supergroup in South Africa. Glacial sediments of the Makganyene Diamictite Formation (corresponding to the Paleoproterozoic snowball Earth event) is overlain by the Hotazel Formation (Fe-Mn ore deposits), with lava flows of the Ongeluk Formation between them. Oxidation of Fe and Mn owing to a rise of O<sub>2</sub> is suggested to have occurred just after the Paleoproterozoic snowball Earth event, at around 2.2 Ga.

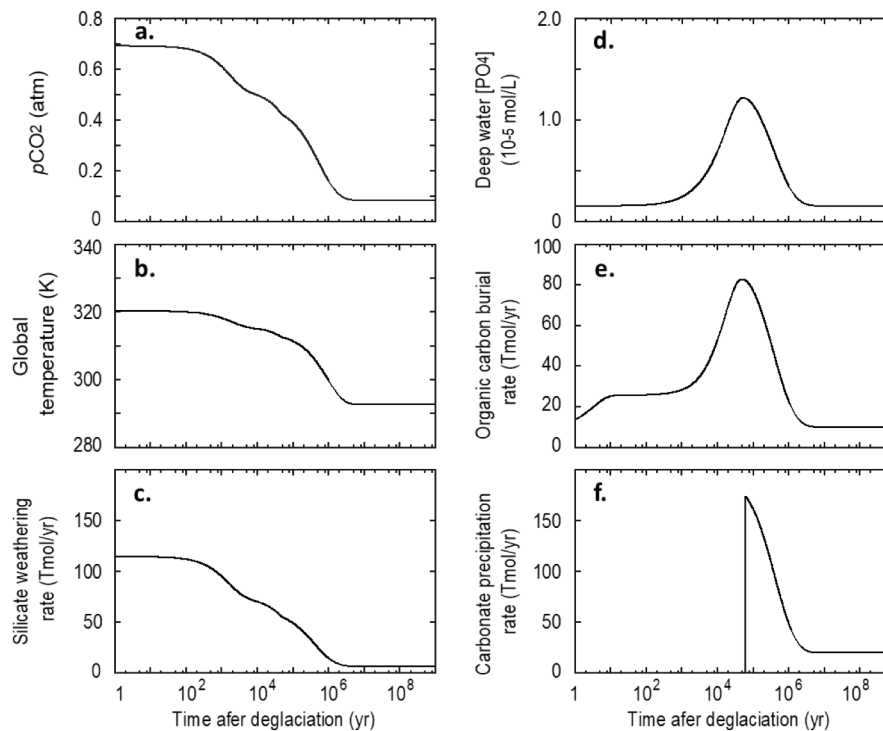
[19, 20]. Intense chemical weathering of continental rocks occurs owing to its temperature dependency, which results in a drawdown of  $\text{CO}_2$  through precipitation of carbonate minerals in the oceans [e.g., 20]. Chemical weathering would deliver a large quantity of bio-limiting nutrients, such as phosphorus, from the continents to the oceans, resulting in blooming of cyanobacteria to produce a large amount of  $\text{O}_2$  to the atmosphere.

We modeled a coupled system of atmospheric photochemistry-climate-biogeochemical cycles to understand theoretical consequence of termination of the Paleoproterozoic snowball Earth event which may have caused the rise of  $\text{O}_2$  in the atmosphere [9]. The model includes a redox balance model of Goldblatt et al (2006) [13]. Processes considered are production of  $\text{O}_2$  and methane ( $\text{CH}_4$ ) from marine biosphere, photochemical oxidation of  $\text{CH}_4$  in the atmosphere, hydrogen escape to space, chemical weathering of silicate and carbonate minerals on the continents, oxidative weathering of organic matters on the continents, precipitation of carbonate and burial of organic matters on seafloor, and reductant input to the surface from Earth's interior. Primary productivity, that is, oxygenic photosynthesis of cyanobacteria is assumed to be limited by phosphorus delivered from the continents to the oceans through chemical weathering.

The standard results of variations of  $p\text{CO}_2$ , the surface temperature, chemical weathering rate of silicate minerals, concentration of dissolved phosphate in surface water ( $[\text{PO}_4]$ ), burial rate of organic carbon (which is equivalent to a net production rate of  $\text{O}_2$ ), and precipitation rate of carbonate are shown in Figs. 4. The surface temperature decreases with time, but unusually hot climate ( $>300\text{ K}$ ) continues on the order of  $10^5$  years (Fig. 4b). Because of the dependency of



**Fig. 3** Schematic variations of the surface temperature during the snowball Earth event. The surface temperature becomes up to  $60^\circ\text{C}$  just after the deglaciation, because 0.7 bars of  $\text{CO}_2$  should accumulate in the atmosphere via volcanism until melting of surface ice [e.g., 18, 19].



**Fig. 4** Numerical results of variations of each variable after the termination of the snowball Earth event [9]. (a)  $p\text{CO}_2$ , (b) global surface temperature, (c) chemical weathering rate of silicates, (d) phosphate concentration in deep seawater, (e) burial rate of organic carbon (i.e., net production rate of  $\text{O}_2$ ), and (f) carbonate precipitation rate.

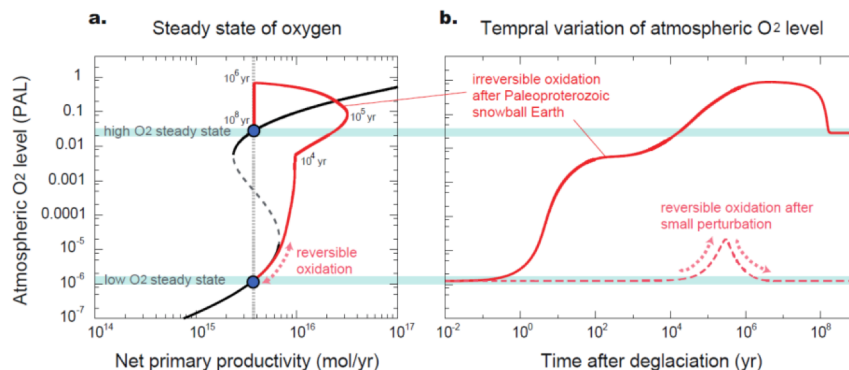


Fig. 5 The numerical results of variations of the atmospheric  $O_2$  levels after the termination of the snowball Earth event [9]. (a) Evolutionary track of the atmospheric  $O_2$  levels superimposed on a bistability diagram between  $O_2$  levels and net primary productivity by Goldblatt et al. (2006) [13]. (b) Time variations of  $O_2$  levels.

chemical weathering reactions on temperature, the rate of chemical weathering of silicate minerals also remains much (ca. 20 times) higher than the present level on the order of  $10^5$  years (Fig. 4c). As a result, a large quantity of phosphates is delivered to the oceans, enhancing  $[PO_4]$  10 times higher than the present level on the order of  $10^4$  years (on the timescale of mean residence time of phosphate in the ocean) (Fig. 4d). It results in an increase in primary productivity of cyanobacteria (hence burial rate of organic carbon; Fig. 4e) 10 times higher than the present level. Burial rate of organic carbon is equivalent to a net production rate of  $O_2$ , hence the atmospheric  $O_2$  levels should increase greatly (Fig. 5).

Transition from low to high stable steady-states of the atmospheric  $O_2$  levels occurs owing to an increase in a net production rate of  $O_2$  one order of magnitude higher than the normal levels (Fig. 5). Interestingly, the  $O_2$  level increases up to 1 PAL in  $10^6$ – $10^7$  years after the termination of the snowball Earth event, and, then, decreases to 0.01 PAL, taking a timescale on the order of  $10^8$  years, representing an overshoot of  $O_2$  levels (Fig. 5).

The overshoot of the atmospheric  $O_2$  levels occurs because the primary productivity becomes one order of magnitude higher than the normal level for a timescale on the order of  $\sim 10^5$  years. Such an exceptionally large perturbation to the carbon biogeochemical cycle system cannot occur usually, but can occur after the termination of snowball Earth events (see [9] for more details).

#### 4. Conclusion

The atmosphere and ocean contains large quantity of  $O_2$  at present because oxygenic photosynthesis of life has been producing  $O_2$  since the emergence of cyanobacteria. However, if there are multiple steady-state levels of  $O_2$  in the atmosphere, it is not easy for the atmospheric  $O_2$

levels to have risen to such a very high levels as seen today. The rise of  $O_2$  requires large-scale perturbation to the system which causes the  $O_2$  production rate to increase one order of magnitude higher than the normal rate. Such an unusually large perturbation could have been caused only by snowball Earth events. In this context, it is suggested that the Paleoproterozoic snowball Earth event has inevitably resulted in the rise of  $O_2$  with an overshoot, which may have promoted biological evolution toward the prosperity of oxygen-dependent life.

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