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 (O2) in the atmosphere may be one of the most critical factors for the evolution
of life during the Earth's history. The concentration of O2 in the atmosphere is 20.9% at present, while
there would have been little O2 in the atmosphere of early Earth. As shown in Fig. 1, the atmospheric
levels of O2 would have risen from < 10^{-5} of the present atmospheric level (PAL) to 10^{-2}-10^{-3} 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].

Oxygencic 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 [7, 8]. Because Mn has a high oxidation
potential, which cannot be oxidized virtually without O2, it is suggested that this would be an
evidence for the rise of O2 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 O2 will be discussed.

Fig. 1 The history of O2 in the atmosphere. The atmospheric O2 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 O2 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 O2 and the rise of
O$_2$ in the atmosphere (i.e., GOE) as described in the previous section. The levels of the atmospheric O$_2$ were stable below $10^{-5}$ PAL before the GOE (>2.4 Ga) [10, 11]. The O$_2$ levels would have been stable around $10^{-2}$-$10^{-3}$ 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$_2$ in the atmosphere is on the order of 10$^8$ years during the Phanerozoic, the stability of the atmospheric O$_2$ levels on the order of 10$^8$ years cannot be explained without some unknown negative feedback mechanisms which stabilize the atmospheric O$_2$ levels. There seems to be multiple (at least, three) stable levels of the atmospheric O$_2$, and the rises of O$_2$ 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$_2$ levels (i.e., a model with two stable O$_2$ levels); one is low ($10^{-2}$ PAL) and the other is high ($10^{-2}$ PAL) atmospheric O$_2$ levels [13]. This is derived from a nonlinear increase in the lifetime of atmospheric O$_2$ due to production of ozone from O$_2$ in the atmosphere. The ozone shields troposphere from ultraviolet (UV) flux from the Sun, because UV flux promotes oxidation of CH$_4$ which consumes O$_2$ at last, once the O$_2$ level exceeds $10^{-5}$ PAL [13]. It is however difficult for the atmospheric O$_2$ 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$_2$ levels ($<10^{-5}$ PAL) have persisted for several hundred million years after the emergence of oxygenic photosynthesis. The reason for the transition of the atmospheric O$_2$ 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 Francavillian Groupe, 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$_2$ levels may have risen more dynamically with an intensive overshoot, up to ~0.1-1 PAL and lasting for ~10$^8$ years (Fig. 1) [1, 15]. Such a dynamical behavior should provide strong constraints on a mechanism and magnitude of reduction-oxidation (redox) budget change during the GOE. Also, it is interesting to note that the rise of O$_2$ 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$_2$ 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$_2$ to accumulate in the atmosphere until the ice melts [17]. A 0.7 bar of CO$_2$ 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$_2$ (Fig. 3).
Intense chemical weathering of continental rocks occurs owing to its temperature dependency, which results in a drawdown of CO₂ 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 O₂ 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 O₂ in the atmosphere [9]. The model includes a redox balance model of Goldblatt et al (2006) [13]. Processes considered are production of O₂ and methane (CH₄) from marine biosphere, photochemical oxidation of CH₄ 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 pCO₂, the surface temperature, chemical weathering rate of silicate minerals, concentration of dissolved phosphate in surface water ([PO₄]), burial rate of organic carbon (which is equivalent to a net production rate of O₂), and precipitation rate of carbonate are shown in Figs. 4. The surface temperature decreases with time, but unusually hot climate (>300 K) continues on the order of 10⁵ 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°C just after the deglaciation, because 0.7 bars of CO₂ should accumulate in the atmosphere via volcanism until melting of surface ice [e.g., 18, 19].](image)

![Fig. 4 Numerical results of variations of each variable after the termination of the snowball Earth event [9]. (a) pCO₂, (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 O₂), and (f) carbonate precipitation rate.](image)
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 10^5-10^7 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 ~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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