

# Paleoproterozoic Atmospheric Oxygenation: Thoughts on causal processes

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The oxygenation of atmosphere and hydrosphere is a unique process to the planet earth and perhaps shaped the evolution of its surface. It is now believed that this oxygenation process initiated at ~ 2.4 Ga as indicated by mass dependent fractionation (MDF) in sulfur isotopes (Farquhar et al., 2000; Bekker et al., 2004). There are many aspects of this important process that remain to be adequately understood. Firstly, the quantitative evolution of atmospheric PO<sub>2</sub> during the Paleoproterozoic has remained elusive so far. Some recent qualitative and semi-quantitative models predict fluctuations in PO<sub>2</sub> levels especially encompassing the probable snow ball earth conditions that characterizes the Paleoproterozoic period (Papineau et al., 2005; Bekker and Kaufman, 2007; Claire et al., 2006). Although there is a consensus that non-MDF disappears at ~ 2.4 Ga, there are many other geological and geochemical evidences that represent higher oxygen levels spanning from as early as 2.7 Ga to 1.85 Ga (Fig. 1). It is difficult to place a higher archival order of these evidences in terms of quantitative PO<sub>2</sub> level, however, the large time span may indicate that oxygen evolution can be quantitatively complex.

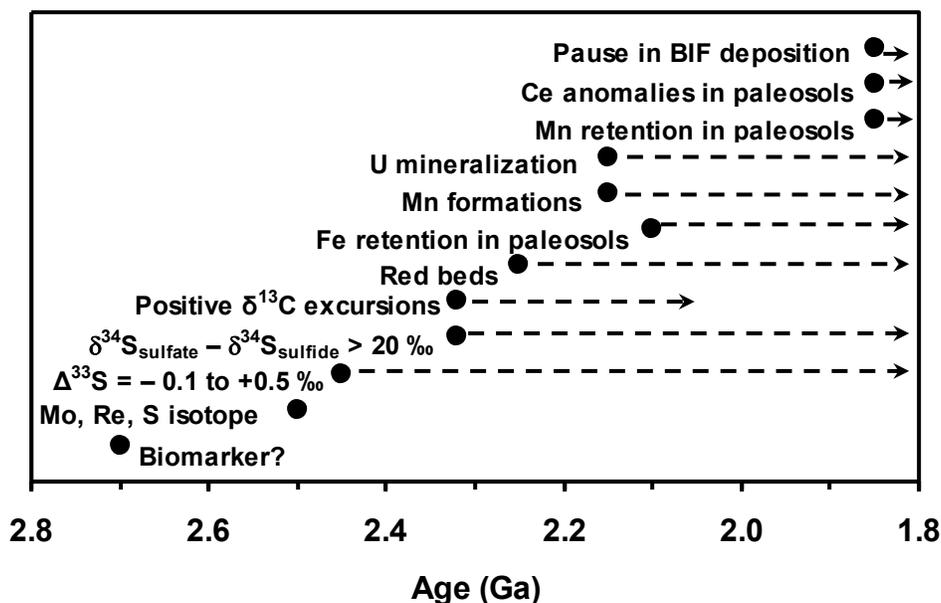


Fig. 1 Geological and geochemical lines of evidence for the presence of increasingly oxygenated conditions during the Late Archean to Paleoproterozoic.

The most important source of molecular oxygen to the atmosphere is the oxygenic photosynthesis. The production rate of oxygen through photosynthesis has to surmount the rate of oxidation of reductants present in the crust and ocean in order to establish and maintain free molecular O<sub>2</sub> in the atmosphere–hydrosphere system. The major reductants that must be oxidized are carbon (as in crust, dead organic matter – byproduct of photosynthesis and

methane), sulfur and metallic ions (chiefly Fe), generated from various sources such as crust, mantle out-gassing during volcanism and low grade metamorphic/hydrothermal alteration. The difference in the rate of oxygen positive feedback and the negative one has in effect determined the pattern as well as the timing of the oxygen rise during the Paleoproterozoic. In the following we examine the role of each of these reductants and the geochemical evidences for their role in the geological record for the possible quantitative evolution of atmospheric PO<sub>2</sub> as well as its causal processes.

1. Carbon: The two important probable forms of carbon as oxygen sinks during the Precambrian are (a) reduced carbon in the crust as well as the organic carbon – a byproduct of photosynthesis and (b) methane in the atmosphere.

(a) Methane (CH<sub>4</sub>): Methane has been proposed to be one of the important greenhouse constituent as the CO<sub>2</sub> levels were predicted to be lower than those required to overcome the reduced solar luminosity during the Precambrian (Rye et al., 1995). Pavlov et al. (2000) have predicted that CH<sub>4</sub> concentration could be > 100 ppm in the Precambrian atmosphere. Presence of such high concentration of methane would inhibit accumulation of free molecular oxygen. It is suggested that the diminishing of methane levels are responsible for not only oxygenation but also the global scale glaciations (snowball earth conditions) during the Paleoproterozoic (Claire et al., 2006). Sreenivas and Das Sharma (2007) have proposed that extreme depletion in δ<sup>13</sup>C values of carbonate carbon in all the lithologies of 2.5 to 2.4 Ga old banded iron formation (BIF) deposits of the Hamersley and Transvaal basins may represent the oxidation of methane. Although such a depletion in methane due to oxidation of methane and removal of resultant CO<sub>2</sub> by BIF precipitation would explain the subsequent glaciations and oxygen rise, it has been proposed that methanogenesis is also dominant during the entire Proterozoic. Thus it may be difficult to predict regarding the timing as well mechanism through which methane became a less influential reductant allowing oxygen accumulation. Recently, it has been found that the Ni/Fe ratios in BIFs start decreasing at ~ 2.5 Ga indicating the Ni-famine affected the methanogens and thereby reducing the methane concentrations (Konhauser et al., 2009). Another possibility is the breakdown of methane under UV radiation in the upper atmosphere to yield carbon and hydrogen and the subsequent escape of the later to space (Catling et al., 2001). However, it still remains to be explained how and when the methane was removed from the atmosphere following which oxygen enriched conditions prevailed.

(b) Organic carbon: Reduced carbon is yet another rapid reductant not allowing the O<sub>2</sub> to accumulate. It is important that the organic carbon should be quickly buried along with sediments so that O<sub>2</sub> buildup can take place. Enhanced organic carbon burial leads to <sup>13</sup>C excursion in carbonate carbon because of preferential retention of <sup>12</sup>C in organic form. Hence, positive excursions in δ<sup>13</sup>C values in 2.32 to 2.06 Ga old carbonate rocks may represent enhanced organic carbon burial, in which case both the timing as well as causative processes of atmospheric oxygenation become apparent. The main constraint on the role of organic carbon burial being responsible for oxygen rise is the condition that it should have been subducted irreversibly. Alternatively it has been proposed that the buried organic carbon has been converted to methane through methanogenesis and the escape of hydrogen to space might have accomplished the O<sub>2</sub> increase (Catling et al., 2001). Apart from the lack of carbon rich rocks in the 2.32 to 2.06 Ga sequences, the oxygen increase appears to have initiated before the <sup>13</sup>C excursion event. Finally, the definite association of this remarkable <sup>13</sup>C excursion with other geochemical evidences for oxygen rise strongly suggests a causal linkage. However, the mechanism through which this process was established has to be studied further.

(2) Iron: Iron in reduced form (Fe<sup>2+</sup>) is an effective sink of oxygen. It can be present both in the oceanic environment as well as crustal regimes. The ferrous iron is mainly produced due to

hydrothermal solutions and considered to be the significant source for Fe in BIFs. One of the remarkable observations of BIFs is their absence for about a billion years from 1.85 to 0.8 Ga. The cessation of BIFs at 1.85 Ga is earlier considered as a result of oxygenation of deep oceans (Cloud, 1972). However, recent studies indicate that it is the sulfur from the bacterial sulfate reduction that might have led to the removal of Fe<sup>2+</sup> from deep ocean (Canfield, 1998). The europium anomalies in BIFs show a gradual increase from Middle Archean to Proterozoic when normalized to BIFs of the 2.5 Ga old Hamersley basin (Sreenivas and Murakami, 2005). This may indicate change in the redox state of the BIF deposition. Importantly, there is a large gap for ~0.4 Ga between 2.4 and 2.0 Ga in the BIF deposition, matching with global glaciations as well as evidences for oxygen enrichment (Canfield, 2005).

The Fe oxidation in crust as indicated by its retention in various Precambrian paleosols shows a gradual rise from 2.5 to 1.85 Ga (Murakami and Sreenivas, under submission). It has been observed that near complete retention of Fe took place in 2.25 Ga Hekpoort paleosols and complete retention of both Fe and Mn in the 1.85 Ga Flin Flon paleosol. Therefore, it can be concluded that Fe in the crust is no longer an inhibitor of oxygen accumulation at least since 2.25 Ga and definitely by 1.85 Ga. The Fe isotope compositions of Precambrian paleosols also corroborate such a proposition (Sreenivas et al., 2009).

(3) Sulfur: The difference in the S isotope compositions of sulfate and sulfide in the geological record can indicate the timing of oxidation of sulfur in the crust (Canfield, 1998). This is mainly because bacterial sulfate reduction induces large fractionation in the reduced sulfur. Although the contribution of crustal sulfur may not be large when compared to Fe it may have played an important role coupled with the sulfide that gets generated through hydrothermal sources in providing potential remover of Fe<sup>2+</sup> from deep ocean inhibiting a major sink of oxygen from active realm. There are clear indications from S isotope record that bacterial sulfate reduction was initiated with the beginning of the Paleoproterozoic (Canfield, 1998). The lack of BIFs between 2.4 to 2.0 Ga – the most crucial time window for the oxygen increase is because of the increased sulfate concentrations or due to some other factors is not yet clarified. It is evident from the above that the biogeochemistry of sulfur played a vital role in the period during which oxygen rise took place.

In summary, the oxygen increase in the earth's atmosphere-hydrosphere system appears to be complex and is a result of interaction among atmosphere, hydrosphere, biosphere and lithosphere. It is essential to look at the various possible interactions and exchanges between the sources and sinks of oxygen in order to understand this intricate process.

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