

Abstract # 12681 - What Caused the Second Rise of O₂ in the Late Proterozoic? Methane, Sulfate, and Irreversible Oxidation

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Several hypotheses have been suggested for a rise of oxygen at 2.2-2.4 Ga, in the early Proterozoic. These include temporary and secular increases in organic burial rates (Karhu and Holland, 1996; Des Marais et al., 1992), oxidation from hydrogen escape to space via biogenic methane (Catling et al., 2001), and a shift in the redox state of volcanic gases (Kasting et al., 1993; Holland, 2002). However, despite evidence that O₂ levels increased a second time in the late Proterozoic, few ideas have been presented to explain why such a second event would occur. Sulfur isotopes suggest that O₂ increased from about 1-3% to greater than 5-18% of present levels around ~0.8 Ga (Canfield and Teske, 1996). At this time, sulfides are found with ³⁴S-depletions exceeding the fractionation threshold of sulfate-reducing bacteria. This can be explained if sulfide was re-oxidized at the sediment-water interface to SO₄²⁻ and reduced again by microbes, cyclically increasing the isotope fractionation. Possibly, O₂ increased to the point where it penetrated marine sediments, making the deep ocean aerobic for the first time. Such a second increase cannot be explained by the evolution of fecal pellets giving a greater flux of carbon to the seafloor (Logan et al., 1995) because the fecal pellets are found near the Cambrian boundary (Walter, 1995), well after ~0.8 Ga.

We suggest that over the course of Earth history, atmospheric CH₄ concentrations have basically reflected the inverse of concentrations of atmospheric O₂ and ocean SO₄²⁻. Today, upward diffusion of CH₄ from seafloor sediments is in approximate steady-state balance with SO₄²⁻ reduction at the CH₄-SO₄²⁻ transition zone (D'Hondt et al., 2002). In the low sulfate Archean ocean, the CH₄ flux would have been less impeded in reaching the atmosphere. In the Mesoproterozoic, sulfate levels were probably only a few mM, compared to 29 mM today (Shen et al., 2002). Thus a substantial flux of CH₄ to the atmosphere likely occurred throughout the Mesoproterozoic. Since CH₄ concentrations vary quadratically with methane flux to the atmosphere (Walker, 1977, p.90), CH₄ was likely an important greenhouse gas not just in the Archean (as argued previously (Catling et al., 2001)), but also in the Proterozoic, when tens of ppmv were likely sustained.

The redox consequences of abundant CH₄ are obvious. Today, biogenic CH₄ contributes about half of the hydrogen atoms that escape to space. With an elevated concentration of CH₄, the CH₄-induced hydrogen escape rate is proportionately greater. When hydrogen escapes from Earth, the Earth must be oxidized. We propose that methane-induced hydrogen escape oxidized the Proterozoic Earth. This oxidation caused a shift in Earth's sulfur cycle towards a sulfate-rich ocean. In the Neoproterozoic, the loss of CH₄ and increased O₂ likely precipitated global cooling and "Snowball Earth" glacial episodes, analogous to those of the Paleoproterozoic.

If the Proterozoic ocean was deeply sulfidic as proposed by Canfield (1998), it is also likely that biogenic sulfides were permanently subducted from the Proterozoic ocean into the mantle, given the highly refractory nature of sulfides. This would also have been a net reductant loss from the atmosphere-ocean-crust system, analogous in its effect to hydrogen escape to space. Thus, the Proterozoic environment was prone to oxidize both from methane-induced hydrogen escape and sulfide subduction.

An interesting question is the regulation of the O₂ content of the Proterozoic atmosphere. With Mesoproterozoic O₂ levels only 1-3% of present, the microbial biosphere would be close to the Pasteur point where a fall in O₂ levels would cause a switch to anaerobic metabolism. Thus it is possible that the biosphere behaved as an important negative feedback on Proterozoic O₂ levels. Today, this control no longer exists because the amount of organic carbon in the biosphere is ~10² times smaller than the atmospheric reservoir of O₂ so that respiration and decay can modulate no more than 1% of total amount of present-day O₂.

In summary, we propose that the redox history of the Proterozoic was one of secular oxidation enabled by methane-induced hydrogen escape and/or sulfide subduction. Oxidation resulted in a second rise of O₂, which was a critical influence on subsequent biology.

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