

Was the Archean atmosphere reducing? Was the Archean atmosphere reducing?

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The current paradigm postulates the following scenarios for the evolution of the atmosphere and oceans: Oxygenic photoautotrophs evolved at ~2.7 Ga, but the atmosphere and oceans remained reducing (i.e., $p\text{H}_2 > 10^{-6}\text{atm} > p\text{O}_2$) until the 'Great Oxidation Event (G.O.E.)' at ~2.45 Ga when the atmospheric $p\text{O}_2$ dramatically rose to ~10% PAL and the ocean surface layer became oxygenated, while the deep oceans remained anoxic. Previous researchers have presented the following observations in some (but not all) Archean-aged rocks to support this paradigm: (a) loss of Fe from paleosols; (b) abundance of banded iron formations (BIFs); (c) presence of 'detrital' grains of uraninite and pyrite; (d) lack of U- and Mo enrichments in black shales; (e) presence of anomalous isotopic fractionations (AIF or MIF) of sulfur in shales and barite beds; (f) presence of unusual isotopic compositions of N and Fe in sedimentary rocks. However, none of these observations are unequivocal evidence for a reducing Archean atmosphere, since all these characteristics have also been found in younger rocks. We have also demonstrated experimentally that the AIF-S signatures, which were previously linked to the UV photolysis of volcanic SO_2 in an O_2 - and O_3 -free atmosphere, can occur during thermochemical sulfate reduction by solid organic matter. We can better explain the above characteristics (c)-(f) by diagenetic, hydrothermal, and metamorphic processes, rather than by atmospheric processes.

In an anaerobic world under a reducing atmosphere, organic synthesis would have occurred through anoxygenic photoautotrophy (e.g., $\text{CO}_2 + 2\text{H}_2 \Rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$), and the decomposition of the organic matter by fermentation (e.g., $\text{CH}_2\text{O} \Rightarrow \text{CO} + \text{H}_2$ and $3\text{CH}_2\text{O} \Rightarrow 2\text{CO} + \text{CH}_4 + \text{H}_2\text{O}$). As the atmospheric CO_2 was converted to reduced C compounds (CO , CH_4 , and C) and not completely recycled back to CO_2 , the atmospheric CO_2 would have continuously decreased, even with continuous supplies of CO_2 by volcanic gas and weathering of carbonates; CO_2 would have disappeared in <~100 million years since the emergence of anoxygenic photoautotrophs and created an icy, dead planet. But this did not happen. The maintenance of a CO_2 -rich atmosphere and the life on Earth through geologic history would have required the recycling of organic matter by aerobic organisms.

A small, but growing, number of researchers postulate that the emergence of oxygenic photoautotrophs and the development of a fully-oxygenated atmosphere-ocean system took place before ~3.5 Ga. They cite the following similarities between Archean and Phanerozoic rocks to support their model: (i) the ranges of organic-C and pyrite-S contents in shales; (ii) the common $\delta^{13}\text{C}$ values of carbonates and shales; (iii) the abundance of sulfate-rich rocks; (iv) the wide $\delta^{34}\text{S}$ ranges for pyrite and sulfates in sedimentary rocks and ore deposits; (v) the common $\delta^{15}\text{N}$ values of shales and cherts; (vi) the Fe, Mo and Cr isotope values of sedimentary rocks; and (vii) the behaviors of various redox sensitive elements (e.g., Fe, Mn, U, Mo, W, As, Ce) in paleosols, BIFs, and hydrothermally-altered submarine basalts.

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