

PLANETARY OXIDATION AND OTHER UNSOLVED RIDDLES. Friedemann T. Freund, SETI Institute, Carl Sagan Center, 189 Bernardo Ave, Suite 200, Mountain View, CA 94043, USA friedemann.t.freund@nasa.gov.

Introduction: It is widely believed that the Great Oxidation Event (GOE) some 2.4-2.7 GYrs ago was made possible by microorganisms, presumably cyanobacteria, that had “discovered” oxygenic photosynthesis and started to inject large amounts of O_2 into the Earth atmosphere. While this is a grandiose idea, Gaia-inspired, it leaves several questions unanswered that are critical for understanding the role of oxygen in the evolution of Life.

These questions are: (i) isn't oxygen highly toxic to primitive forms of Life that formed in the pervasively reduced environment of the early Earth? (ii) How can primitive organisms, had which supposedly never experience anything but a reducing environment, suddenly “invent” the complex biochemistry that is necessary to deal with pernicious O_2 and to use free O_2 to run a more efficacious energy-producing metabolism? (iii) How can it be rationalized that the geological record provides evidence for early oxidation before the GOE?

Despite the near-universal acceptance in the science community of a biological origin of O_2 in Earth's atmosphere, the question must be allowed whether this Gaia-inspired idea is really supported by the evidence and whether an alternative source of free O_2 may exist, an abiotic source for free O_2 rooted in geology.

Evolutionary changes in biology never happen without a reason. Major changes always occur in incremental steps driven by selective pressure towards adaptation to changing environments. The universal laws of Natural Selection surely apply to such a fundamental change in the basic machinery of Life as the transition from reducing to oxidizing conditions. Hence, before early microorganism were able to use potentially lethal O_2 to their benefit and even produce O_2 as part of their metabolism, they first had to learn how to cope with the presence of O_2 .

It therefore stands to reason to doubt the validity of belief that the transition from reducing to oxidizing conditions during GOE was made possible by microorganisms having “invented” oxygenic photosynthesis. No microorganisms would have been able to do so without evolutionary pressure provided, for instance, by a trend toward an ever increasing oxidation imposed by the geological environment. Such a scenario is supported by the observation that one of the genetically oldest antioxidant enzymes, superoxide dismutases, is found in prokaryotes, which are among the oldest and most primitive microorganisms that evolved more than a GYr before GOE and before the O_2 -tolerant eukaryotes.

Discussion: Thermodynamics mandates that all minerals that crystallize from an H_2O -laden magma incorporate some H_2O in solid solution, commonly in the form of impurity hydroxyls such as OH^- or $Si-OH$. During cooling, the hydroxyls exsolve up to the point, when diffusional processes become so sluggish, that the system can no longer maintain thermodynamic equilibrium. Around $500^\circ C$ a redox conversion takes place, in the course of which pairs of hydroxyls rearrange electronically: the two H reduce from H^+ to H^0 , forming H_2 , while the two O oxidize from O^{2-} to O^- forming peroxy: $Si-OHHO-Si \Leftrightarrow Si-OO-Si + H_2$.

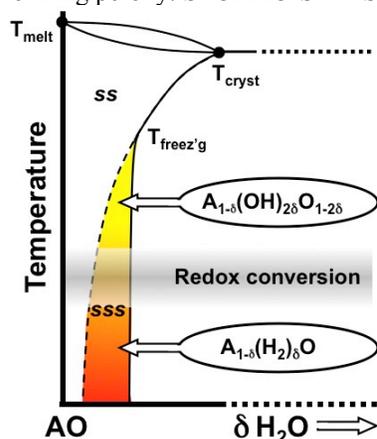


Figure 1: Binary AO- H_2O phase diagram: ss stands for “solid solution”, sss for “supersaturated solid solution”. In the sss state, under metastable conditions, the redox conversion generates peroxy bonds plus H_2 [1].

As a result of this redox conversion igneous rocks and high-grade metamorphic rocks are “loaded” with H_2 on interstitial sites in the constituent minerals [2]. Inside the minerals peroxy's lurk. H_2 and peroxy defects are inconspicuous and have indeed been widely overlooked – ignored – by the geoscience community. At present little is known how much H_2 and peroxy is present in typical crustal rocks. Concentration levels on the order of 1000 ppm may be typical [3].

While the reaction $Si-OHHO-Si \Leftrightarrow Si-OO-Si + H_2$ is reversible at elevated temperatures, the H_2 molecules are diffusively mobile, even in dense mineral structures, making this reaction unidirectional. In addition, H_2 can outdiffuse from the mineral matrix, in which they were produced, enter the intergranular space and get lost to either H_2 -consuming microbes in the deep biosphere or to space [2].

Importantly, H_2 will no longer react with peroxy during weathering at Earth surface temperatures. Instead the peroxy bonds hydrolyze to produce hydrogen peroxide: $Si-OO-Si + H_2O \Rightarrow 2 Si-OH + H_2O_2$ [4]. Since H_2O_2 decomposes to $H_2O + \frac{1}{2} O_2$, it can carry out other oxidation reactions such as, for instance, oxidizing ferrous iron, Fe^{2+} , co-released during weather-

ing, to ferric, Fe^{3+} , precipitating it in form of Fe^{3+} -bearing minerals such as FeOOH and/or Fe_2O_3 .

As long as the geoscience community did not take notice of the redox conversion by which solute hydroxyls in rock-forming minerals turn into H_2 plus peroxy, the oxidation potential of rocks during weathering could not be assessed. Therefore it was unknown that weathering can lead to oxidation beyond the thermodynamically controlled redox couple of, for instance, $\text{Fe}^{2+}/\text{Fe}^{3+}$ in aqueous solution.

If average peroxy concentrations in common rocks are on the order of 1000 ppm, weathering of every km^3 will inject approximately 2×10^{12} g free oxygen into the Earth's surface environment. Today's weathering rate is about $3 \text{ km}^3/\text{yr}$. Assuming that the weathering rate on the early Earth was higher by a factor of 2 (a very conservative estimate), the amount of free O_2 injected into the early Earth's environment via this mechanism would have been on the order of 10^{13} g/yr.

Obviously, all of this oxidizing potential would first have been consumed to oxidize sinks such as Fe^{2+} and other reduced transition metals as well as sulfur co-released during weathering. After 1-2 GYr, as the continental rocks became ever more granitic-andesitic [5]{Rudnick, 2013 #3996}, weathering of rocks would release lesser amounts of Fe^{2+} and other reduced components. At this point peroxy defects would have become available in the near-surface environment, the habitat of early life forms. The microorganisms would then have been exposed to highly reactive, highly oxidizing radicals such as produced during Si-OO-Si hydrolysis, in particular $\bullet\text{O}$ and $\bullet\text{OH}$ [6, 7].

This scenario suggests that early life must have been under continuous attack by Reactive Oxygen Species (ROS) during the weathering of rocks. They would have been under evolutionary pressure to develop enzymatic defenses such as superoxide dismutase, an anti-oxidant already found in prokaryotes [7, 8].

We might thus expect that, after a lengthy period of time – possibly hundreds of millions of years – some microorganisms would become adapted to the oxidative assault in their environment by developing a new biochemical machinery, which allowed them to not only cope with free O_2 but to use O_2 to their advantage.

Such a scenario of a plausible path towards oxygenic photosynthesis implies that this major step in the evolution of Earth's biosphere was driven by a purely geological process. The Gaia-inspired idea that Life can have a profound effect on the evolution of the planet as a whole would then apply to the subsequent time, when photosynthesis started to inject massive amounts of free O_2 into Earth's atmosphere.

The processes which lead to the introduction of peroxy into rocks are universal [9]. Therefore, wherever

Life might have started on some other planetary body under conditions not too dissimilar to Earth's, its evolution will be marked by the same evolutionary pressure from highly oxidizing as outlined here.

The presence of peroxy in rocks is important also in other respects, in particular in geophysics. The reason is that, when peroxy defects break up, electronic charge carriers are generated, electrons and holes. One way of achieving the break-up is through mechanical stress such as produce in the Earth's crust prior to earthquakes. The electrons remain in the stressed rock volume, while the holes have the remarkable ability to flow out of the stressed rock volume, into the adjacent less stressed or unstressed rocks. The holes propagate fast and far, at speeds up to 100 m/s and over distances on the order of tens of kilometers [10]. Because of their unusual properties they are called positive holes.

Deciphering these processes has led to profound changes in the understanding of earthquake and pre-earthquake phenomena [11].

When the positive holes arrive at the Earth surface, they cause a variety of follow-on reactions. For instance, they can recombine returning to the peroxy state. In the process energy is released, which leads to vibrationally highly excited surface atoms and the emission of spectroscopically distinct infrared photons in the region of the thermal infrared (TIR) bands – a process that is also of interest in the context of pre-earthquake science [12, 13].

Monitoring the TIR emission by satellite-based remote sensing may be a useful method to identify deep interior stresses waxing and waning on Mars.

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