An Alternative Explanation for the Great Oxygenation Event (GOE): Weathering of Rocks Containing Minerals with Peroxy Bonds

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Abstract

During the Great Oxygenation Event (GOE) 2.4 - 2.35 Gyrs ago, Earth experienced a notable shift in its oxidation state. This has been widely attributed to cyanobacteria having "invented" oxygenic photosynthesis. We present a very different view based on the fact that oxygen is released from rocks during weathering. If so, the GOE must have been caused by an influx of abiogenic O_2 into Earth's surface environment. Minerals forming Earth's crust contain impurity hydroxyls such as O_3SiOH. Pairs of those are known to undergo a common redox conversion, ubiquitously forming peroxy defects plus H_2:

$O_3SiOH\text{-}HOSiO_3 = O_3Si/^{OO}\backslash SiO_3 + H_2$

Being diffusively mobile, most H2 will be lost, leaving behind bound O as peroxy. The peroxy defects release O_2 during weathering:

$O_3Si/^{OO}\backslash SiO_3 + H2O \rightarrow O_3SiOH\text{-}HOSiO_3 + \frac{1}{2}\ O_2$

We suggest that this abiogenically generated O_2 was responsible for the progressive oxidation of the early Earth and that this abiotic process drove the Great Oxygenation Event (GOE).

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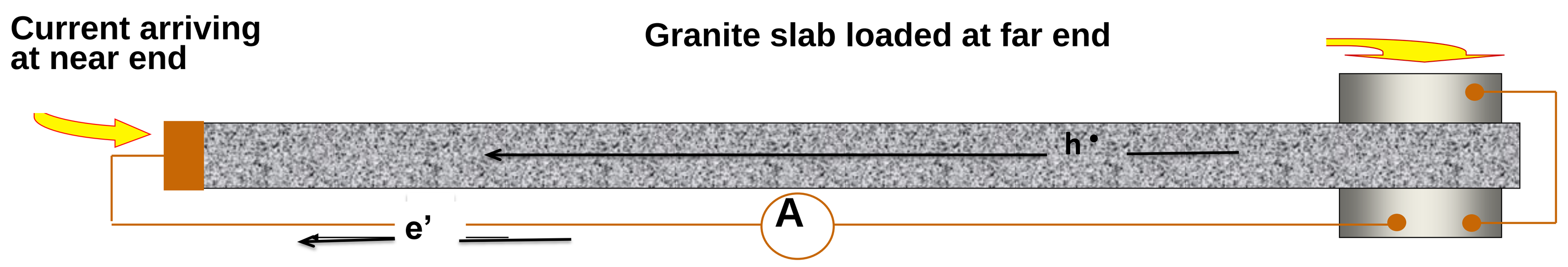
$$O_3Si/^{OO}\backslash SiO_3 + H_2O \Rightarrow O_3SiOH\text{-}HOSiO_3 + {}^1/_2\, O_2$$

We suggest that this abiogenically generated O_2 was responsible for the progressive oxidation of the early Earth and that this abiotic process drove the Great Oxygenation Event (GOE).

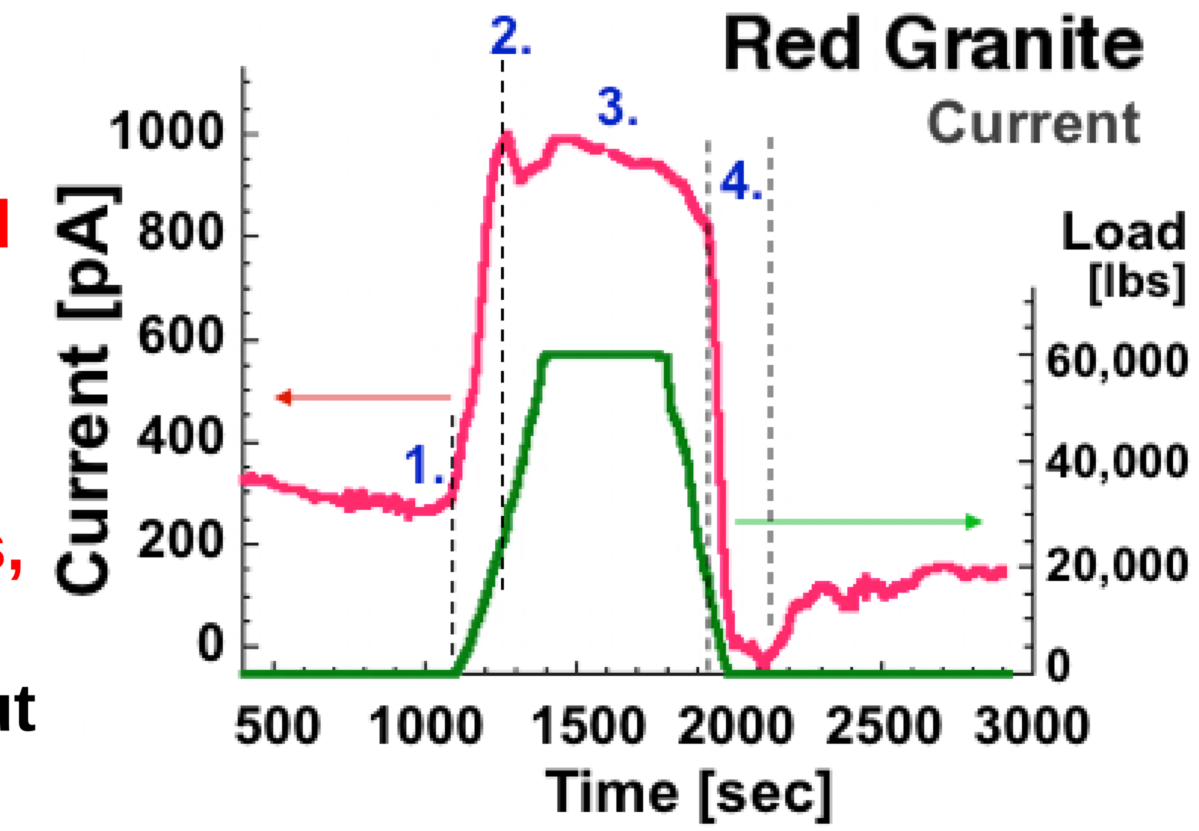
Challenge

How Earth became oxidized and how oxygen became a major part of Earth's atmosphere is still hotly contested. The main problem is that no known process seemed capable to explain the introduction of O_2 by purely abiotic means. Thus, only a biogenic origin of O_2 seemed plausible. Understandably, this led to the idea that oxygenic photosynthesis must have been "invented" early in Earth's history, maybe by photosynthetic cyanobacteria.



Upon stressing one end of this granite slab, an electric current starts to flow – highly unexpected and unusual.

This current has been shown to flow for hours, days, even months, decreasing exponentially. Upon unloading it disappears rapidly, but reappears upon reloading.



Experimental Observation

When we mechanically stress a granite slab, 4 m long as shown above, we should not observe any changes in the electrical properties of this rock.

However, as depicted above on the right, as soon as a load is applied to the far end of this 4 m slab, an electric current starts to flow, flowing through its full length, growing with the load as shown above on the right, passing through a maximum, decreasing first at constant load and then rapidly upon unloading.

This stress-induced current is positive, indicating that its charge carriers are positive. These charge carriers have been identified as defect electrons in the O^{2-} sub-lattice, hence O^- in the O^{2-} matrix, known as positive holes. They derive from peroxy defects in the matrix of mineral grains and along their grain-grain contacts:

$$O_3Si/^{OO}\backslash SiO_3 + O^{2-} \rightarrow O_3Si/^{O\bullet O}\backslash SiO_3 + O^- \;(h^\bullet)$$

Peroxy defects exist in Earth's crust at estimated concentrations of 100–1000 ppm. They are, in fact, excess oxygen and release O_2 during weathering:

$$O_3Si/^{OO}\backslash SiO_3 + H_2O \rightarrow O_3SiOH\text{-}HOSiO_3 + {}^1/_2\, O_2$$

Note that this O_2–producing process is purely abiotic.

Abiogenic Oxygen

Today's global weathering rate is ~3 km^3/yr. Early in Earth's history, the weathering rate was certainly higher, maybe ~10 km^3/yr. Assuming a peroxy content of 100–1000 ppm in average rocks, the amount of abiogenic O_2 injected into the early Earth's surface environment was 8.4×10^{10}–8.4×10^{11} mol/yr, equivalent to 2.7×10^{12} –2.7×10^{13} g O_2/yr.

Effect on Early Life

Positive holes are highly reactive and oxidizing. They are released not only through weathering but also become activated by tectonic stress. They travel through Earth's crust as highly mobile $h^\bullet$ charge carriers. When they enter bodies of water, they turn into •OH radicals and H_2O_2. Therefore, $h^\bullet$ certainly challenged early lifeforms. In response, ever since Life appeared on Earth the early lifeforms must already have developed defense mechanisms to survive highly oxidizing conditions.

Conclusions

We propose that, before oxygenic photosynthesis could develop, early lifeforms had to learn – and did learn – how to survive the oxidizing conditions created by the omnipresence of highly oxidizing $h^\bullet$ in Earth's crust. Only then could early Life take advantage of the energy gain afforded by the development of oxygenic photosynthesis.

References

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Freund, F.T., Ouillon, G., Scoville, J., Sornette, D.: Eur. Phys. J. 230, 7–46 (2021)