IS THERE NOTHING ELSE TO OXIDIZE THE EARLY EARTH BUT OXYGENIC PHOTOSYNTHESIS?

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Introduction: The call for this session starts with the sentence: "*Earth's three major geologic eons (the Archean, Proterozoic, and Phanerozoic) have become nearly synonymous with differing partial pressures of atmospheric oxygen…*" but continues to say *"… a waste product of cyanobacteria*." This last statement foreordains the belief that the early Earth became oxidized over the course of the first 2 ½ GYrs through the action of early microorganisms, which "invented" oxygenic photogenesis.

How the Earth turned from a pervasively reduced state into a surfically oxidized planetary body has been discussed intensely for many years (*1-6*). While there is growing evidence for a Great Oxidation event about 2.4-2.5 GYr ago, during which the oxygen partial pressure rose dramatically to near-present atmospheric levels (*7-9*), the eon of interest here is the time preceding the Great Oxidation event, the Archean. During the Archean the overall oxygen partial pressures were very low to low but there must have been a continuous input of oxidative power as evidenced in the paleosol record (*2, 10*) and by the worldwide deposition of Banded Iron Formations (*11*).

The scientific community evaluated every imaginable physical and chemical process, which could have led to global oxidation, and reached a consensus, though not unanimous, that there is no known physico-chemical process, which "could have done the job". Hence the idea, almost by default, that the oxidation of the early Earth must have been achieved by biological activity.

New Insight: We have recently described a physico-chemical oxidation process, which is a strong candidate for the global oxidation of the early Earth (*12*). It is based on the discovery of electronic charge carriers in rocks, which had not been previously recognized. These charge carriers are defect electrons in the oxygen anion sublattice, O^- in a matrix of O^{2-}, known as positive holes. They normally lie dormant, as positive hole pairs, equivalent to peroxy links, O_3Si-OO-SiO_3. The peroxy links are inconspicuous point defects in the structure of many rock-forming minerals that have crystallized from H_2O–laden magmas or recrystallized in high-temperature H_2O–laden metamorphic environments (*13*). They are electrically inactive, but when rocks are subjected to stress, the peroxy links break and release positive holes.

$$O_3Si/^{OO}\backslash SiO_3 + O^{2-} = O_3Si/^{O}\bullet_{O}/SiO_3 + O^- \quad [1]$$

Eq. [1] illustrates this process. It involves as its crucial step an electron transfer from an outside O^{2-} into the broken peroxy link. The donor O^{2-}turns into O^-, a defect electron on the oxygen anion sublattice or positive hole, chemically an O^- in a matrix of O^{2-}.

These positive holes are highly mobile and long-lived. Once activated, they stay "awake" for weeks and months. As electronic charge carriers they move through rocks by successive electron transfers from O^{2-} to O^- at phase velocities up to 200 m/sec. They have the unusual capacity to travel along stress gradients, from stressed rocks into unstressed rocks, traversing meters of rock in laboratory experiments, most likely km's to tens of km's in the field. When they encounter a rock-water interface, they change from electronic charge carriers to •O radicals, capable of oxidizing H_2O to H_2O_2:

$$[O^-]_{surface} + [H_2O]_{liquid} = [OH^-]_{surface} + [\bullet OH]_{liquid}$$
$$2\ \bullet OH \rightarrow H_2O_2$$

This H_2O oxidation is stoichiometric with two positive holes producing one H_2O_2 molecule (*12*). Two H_2O_2 decompose to produce one O_2 molecule: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$.

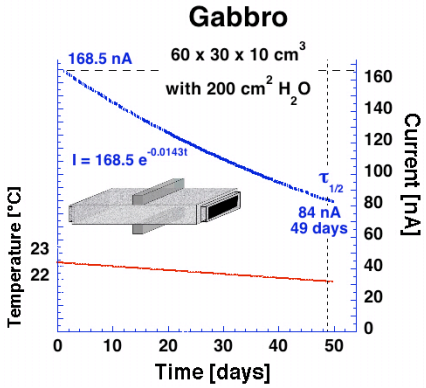

Fig. 1 illustrates how we create a stress gradient in the laboratory by loading a gabbro, 60x30x10 cm^3, along the center line between two rectangular pistons and measure the current flowing from the stressed rock volume to both ends, where we have attached water baths with Cu electrodes. Applying a stress equivalent to less than 5% the fracture strength and holding it constant for nearly two months generates a

positive hole current of nearly 170 nAmp, which decays with a half life of ~50 days. The current density is on the order of 1 nAmp/cm^2. Higher temperatures, higher stresses or stresses, which increase with time, yield higher current densities, up to 100 nAmp/cm^2. If we linearly extrapolate these values to larger cross sections, say km^2, the total currents would be expected to reach 1-100 Amp/km^2.

Application to Early Earth: We know that for every two positive hole charge carriers crossing the rock-water interface one H_2O_2 molecule is formed. For every two H_2O_2 molecules, one O_2 is released. With this basic knowledge we can now proceed to estimate the positive hole currents flowing in the Earth's crust under realistic geophysical conditions.

Every mountain building process is accompanied by far-reaching and sustained tectonic stresses and stress gradients. Often mountain chains pile up in the thrust direction of large continental collision and subduction zones. Examples on today's Earth are the mountains extending from the Alps to the Himalayas and the Andes.

We assume that a stress gradient exists along a length of 10,000 km and a positive hole current flows through a 10 km deep layer. This gives a cross section of 10^5 km^2. If we assume a current density of 1-100 Amp/km^2, the current will be 10^5 to 10^7 Amp. With 1 Amp = 1 Coulomb/sec this is equivalent to about 10^{11}-10^{13} Coulomb per year. Approximately 10^5 Coulomb produce 1 mole H_2O_2. Therefore the amount of O_2 injected into the near-surface environment due to this stress-activated positive hole current along a mountain chain of about 10,000 km length will be 10^6-10^8 mole/yr.

For this first analysis we have chosen very conservative values. Further work will be needed to validate the oxidation processes carried out by stress-activated positive hole current on a dynamic planet like Earth.

Unraveling the story of oxygen will indeed require strong interdisciplinary effort.

References:

1. J. C. G. Walker *et al.*, in *Earth's Earliest Biosphere,* J. W. Schopf, Ed. (Princeton Univ. Press, Princeton, NJ, 1983), pp. 260-290.
2. H. D. Holland, *The Chemical Evolution of the Atmosphere and Oceans*. (Princeton University Press, Princeton, NJ, 1984), pp. 582.
3. J. S. Levine, *Origins of Life* **16**, 203 (1986).
4. K. M. Towe, *Nature* **348**, 54 (1990).
5. J. F. Kasting, *Science* **259**, 920 (1993).
6. D. E. Canfield, *Nature* **400**, 503 (1999).
7. H. D. Holland, *Geochim Cosmochim Acta* **66**, 3811 (2002).
8. A. D. Anbar *et al.*, *Science* **317**, 1903 (2007).
9. A. L. Sessions, D. M. Doughty, P. V. Welander, R. E. Summons, D. K. Newman, *Current Biology* **19**, R567 (2009).
10. W. Yang, H. D. Holland, R. Rye, *Geochim Cosmochim Acta* **66**, 3707 (2002).
11. S. E. Kesler, H. Ohmoto, Eds., *Evolution of Early Earthís Atmosphere, Hydrosphere, and Biosphere: Constraints from Ore Deposits*, vol. Memoir 198 (MWR198) (GSA Bookstore, 2006), vol. Memoir 198 (MWR198), pp. 331.
12. M. Balk *et al.*, *Earth Planet. Sci. Lett.* **283**, 87 (2009).
13. F. Freund, *Journal of Non-Crystalline Solids* **71**, 195 (1985).

Acknowledgment: Supported by NASA Exobiology Progam