How Water Helped Oxidizing the Earth – the Peroxy Way

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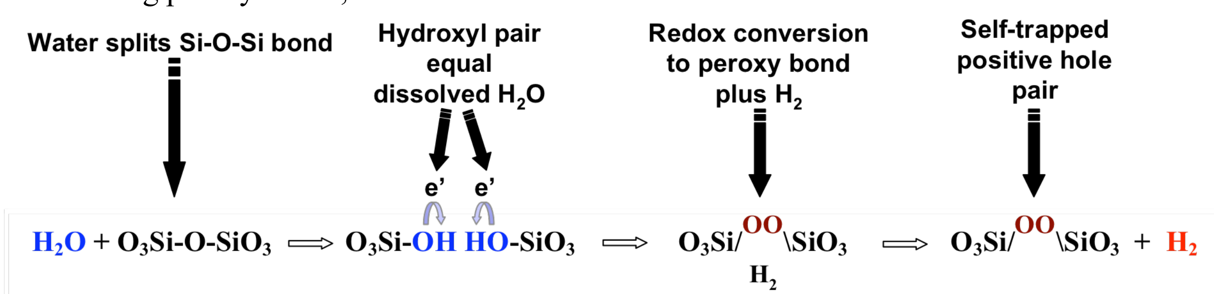
We live on a planetary body with an oxygen-rich atmosphere. We forget that this is an anomaly in the solar system and beyond. Originally, accreting out of the H-dominated solar nebula, the entire Earth was thoroughly reduced. However, over the course of Earth's first 1.5 to 2 billion years, oceans and the surface environment became slowly, but inextricably ever more oxidized. Still there was little or no free O_2 in the atmosphere. About 2.4 billion years ago the global oxidation accelerated, leading to what is known as the "Great Oxidation Event". After that remarkable event, the Earth's atmosphere acquired the 21 vol-% of free O_2, which we now enjoy.

Most likely the "Great Oxidation Event" marks the rise of oxygenic photosynthesis: Life's capacity, with the help of sunlight, to split H_2O and CO_2 into H and organic C plus O_2. By contrast, the cause for the slow but seemingly unstoppable early global oxidation remains essentially unexplained.

It now appears that water had something to do with it, although in a somewhat unexpected way.

When rocks crystallize from magmas or recrystallize deep in the Earth's crust most of their minerals are nominally anhydrous, meaning that their crystal structures do not provide any regular sites for hydroxyl, OH^-.Nonetheless nominally anhydrous minerals invariably incorporate small amounts of H_2O, generally in the form of hydroxyl, Si-OH, commonly Si-OH OH-Si pairs. During cooling, many of these "impurity" Si-OH HO-Si pairs, if not most, rearrange electronically splitting off H_2 and forming peroxy bonds, Si-OO-Si. Chemists call this a redox reaction:



With H_2 being diffusively mobile and capable of escaping over time, terrestrial rocks retain peroxy as a memory of a former solute H_2O content. On the tectonically active early Earth the presence of peroxy in essentially all crustal rocks has far-reaching consequences (even if some H_2 lingers on). During weathering peroxy hydrolyzes to H_2O_2 (hydrogen peroxide). Peroxy bonds under tectonic stresses, break. They generate an electric current carried by defect electrons in the O^{2-} sublattice (positive holes), equivalent to O^- radicals, which oxidize water to H_2O_2 at rock-water interfaces.

Peroxy in rocks may have provided enough oxidation power to change the course of history, forcing the early Earth to slowly oxidize over the course of her first 1.5 to 2 billion years. Along the way reactive oxygen species (ROS), released during the break-up of peroxy, provided a "training ground" for primitive early Life to evolve toward the more advanced eukaryotic life forms. The eukaryots were able to cope with and eventually take advantage of free O_2 in Earth's atmosphere by "learning" how to do oxygenic photosynthesis.