

From evolution of Mn-bearing minerals to photogeochemical cycle of Mn

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Manganese (Mn) oxides have been prevalent on Earth since before the Great Oxidation Event, and the composition and species of manganese minerals presents a deep-time co-evolution relationship with the Earth environment, while the Mn cycle is one of the most important biogeochemical processes on the Earth's surface. In natural environments exposed to sunlight, the photochemistry of manganese oxides can harvest and convert solar energy, splitting water into oxygen under sunlight. One of the most widespread Mn oxides is birnessite, which is a semiconducting layered mineral that actively drives Mn photochemical cycling in Nature. The oxygen-evolving centre in biological photosystem II (PSII) is also a Mn-cluster of Mn_4CaO_5 , which transforms into a birnessite-like structure during the photocatalytic oxygen evolution process. This phenomenon draws the potential parallel of Mn-functioned photoreactions between the organic and inorganic world. The Mn photoredox cycling involves both the photo-oxidation of Mn(II) and the photo-reductive dissolution of Mn(IV/III) oxides. For Mn(II) oxidation into Mn oxides, mechanisms of biological catalysis mediated by microorganisms (such as *Pseudomonas putida* and *Bacillus* species) and abiotic photoreactions by semiconducting minerals or reactive oxygen species have both been proposed. In particular, anaerobic Mn(II) photo-oxidation processes have been demonstrated experimentally, which shed light on Mn oxide emergence before atmospheric oxygenation on Earth. Therefore, manganese oxides are likely to be the embryonic form of photosynthetic OEC, which tightly couples the organic and inorganic worlds in manganese-driven photochemical reactions. As a result, mineral-induced oxygen evolution reactions may have played a parallel role of biological photosynthesis in geological history.