Photon-induced redox chemistry on Earth's surface via semiconducting Mn oxides

YAN LI*, ANHUAI LU, HONGRUI DING, YANZHANG LI, YUWEI LIU, FEIFEI LIU

School of Earth and Space Sciences, Peking University, Beijing, China. (*correspondence: liyan-pku@pku.edu.cn. ahlu@pku.edu.cn, dhr_100@163.com, yzlee@pku.edu.cn, ywliu-pku@pku.edu.cn, qduliufeifei@126.com)

Solar energy is the most abundant and sustainable energy form in nature. The well-known chlorophyll- or rhodopsin-based phototrophy systems enable sustainable solar-to-chemical energy conversion in the organic world. This study identifies a huge natural "solar panel" inherent in the geology of Earth with a role similar in-part to biological phototrophy systems, where an inorganic, mineral system, with vast expanses of rock surfaces exposed to sunlight, are shown to be capable of harvesting and converting solar to chemical energy and therefore driving (bio)geochemistry on Earth's surface. An *in situ* scanning-probe measurement technique is applied to record the photocurrents generated from natural rock-varnish samples. The sample responds with a sensitive and stable photocurrent when exposed to simulated solar light just like a natural photoelectric device. The linear relationship between photocurrent and laser power demonstrates a constant photon-to-electron conversion efficiency. As compared to Fe-rich coating, there is an siginificant enhancement of the effective quantum efficiency for the Mn-rich coating. Coincidentally, Mn-rich mineral coatings are generally found only on upper rock surfaces that are exposed to solar light, and are also observed on the sunlit side of landforms and in high-UV flux environments [1-3]. All these suggest a close relationship between the Mn oxides and solar light. The solar-responsive capability of the Mn-rich mineral coatings is ascribed to the existence of semiconducting birnessite. Considering the wide and vast distribution of dark Mn-rich minerals on Earth's surface, this photon-to-electron conversion function possessed by exposed rocks/soils is clearly very important. It gives the lithosphere the potential to utilize solar energy and transform it into other energy forms that can be available for microorganisms and other geochemical redox reactions even in barren and desert locations.

[1] Schindler & Dorn (2017) *Elements* **13**, 155-158. [2] Nealson (2015) *Env. Microbiol. Rep.* **7**, 33-35. [3] Krinsley *et al.* (2009) *Astrobiology* **9**, 551-562.