Anoxic Conversion of Rhodochrosite to Mn Oxides in the Presence of Ultraviolet Light

WINNIE LIU[1,*] NATHAN YEE[1] EVERT ELZINGA[2] PIOTR PIOTRWIAK[3] VIKAS NANDA[4] PAUL FALKOWSKI[1]

[1]Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ 08854
(*correspondence: winnie.liu@rutgers.edu)
[2]Department of Earth and Environmental Sciences, Rutgers University−Newark, Newark, NJ 07102
[3]Department of Chemistry, Rutgers University−Newark, Newark, NJ 07102
[4]Department of Biochemistry and Molecular Biology, RWJ Medical School–Rutgers, Piscataway, NJ 08854

Introduction: The presence of manganese (III)/(IV) oxides in Archean rocks has been suggested to be a proxy for biological production of atmospheric oxygen [1]. However, photogeochemical reactions caused by UV radiation in an ozone free atmosphere can also influence the redox state of manganese minerals abiologically. The mineral rhodochrosite ($MnCO_3$) is common in Archean manganese deposits and has a band gap in the UV range, indicating a possible photochemical path to manganese oxide formation [2]. In this study, we investigated the photoreaction of rhodochrosite to manganese oxides under anoxic conditions by UV light.

Methods: Rhodochrosite was synthesized in an anaerobic chamber by mixing solutions of $MnCl_2$ and Na_2CO_3. A 450 watt mercury lamp and sealed quartz reaction vessels were used to irradiate the rhodochrosite for 5-11 days. A subset of the product was extracted with acetic acid to remove residual rhodochrosite. Scanning electron microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD), and gas chromatography (GC) were used to analyze the products.

Results and Discussion: The irradiation produced H_2 gas indicating a photon induced redox reaction. The production of H_2 was concurrent with the formation of a dark colored secondary mineral phase. SEM and IR analyses revealed the the formation of a manganese oxyhydroxide, and XRD analyses confirmed the formation of manganite (γ-MnOOH). Manganite can spontaneously disproportionate into MnO_2 and Mn^{2+} over time, providing a plausible mechanism for forming higher valent manganese oxides abiologically in the absence of oxygen [3].

[1] Johnson, Webb, Ma & Fischer (2016), *Geochim. Cosmochim. Acta.* 173, 210–231. [2] Wang, Huang, Lou, Wang, Qin, Zhang & Dai (2016), *Appl. Catal. B Environ.* 180, 6–12. [3] Ramstedt & Sjöberg (2005), *Aquat. Geochemistry.* 11, 413–431.