

Experimental study of Fe^{2+} photo-oxidation in circumneutral-pH solution: Implications for the trigger for acidification of surface water on early Mars

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Mars is suggested to have experienced a global environmental change around the boundary between the Noachian and Hesperian, characterized by a dramatic shift in pH of surface water from circumneutral to highly acidic (Bibring et al., 2006). The previous study has proposed that photo-oxidation of ferrous iron (Fe^{2+}) dissolved in surface water may have caused the acidification (Hurowitz et al., 2010), because this reaction produces proton (H^+) via formation of Fe(III) oxide and H_2 , as follows.



Although this process can explain the mineral assemblages and chemical compositions of Hesperian sedimentary rocks revealed by the Opportunity rover (Rieder et al., 2004, Morris et al., 2006), the trigger for the onset of the photo-oxidation on early Mars remains unclear.

Our previous study has proposed a qualitative hypothesis that a change in the solar irradiance on early Mars could have triggered the shift in pH of surface water (Tabata et al., 2016). More particularly, UV shielding by abundance SO_2 could have inhibited the photo-oxidation reaction; whereas, reaching of solar UV light due to a decline in atmospheric SO_2 level may have caused an acidification. To assess this hypothesis more quantitatively, the reaction rate of the photo-oxidation is necessary. However, the kinetics data obtained by the previous studies are limited only under highly acidic conditions, namely $\text{pH} < 3.0$ (Jortner et al., 1962).

In the present study, we conducted laboratory experiments to measure the Fe^{2+} photo-oxidation rate at $\text{pH} > 3.0$. In the experiments, we irradiated UV and visible light using a Xe lamp onto a Fe^{2+} -containing solution in a quartz reaction vessel. An optical filter was used to control the spectrum of the light source onto the solution. To avoid oxidation of Fe^{2+} by atmospheric O_2 , the preparation processes were performed in a Ar-purged glovebox. The reaction rate was obtained from a gradient of Fe^{2+} concentrations in the solution over the irradiation time.

Our experimental results show that the reaction rate of the photo-oxidation at circumneutral pH is consistent with a predicted value that is calculated from the following empirical equation obtained at $\text{pH} < 3.0$ (Jortner et al., 1962).

This suggests that the reaction mechanism would be independent from pH, at least from acidic to circumneutral values. In addition, our results indicate that UV shielding at wavelength < 300 nm strongly inhibits the photo-oxidation within the solution, implying that surface water with circumneutral pH can be maintained in the presence of UV absorbers in the atmosphere on early Mars. Based on these experiments, we strongly support the hypothesis that a change in the atmospheric composition, namely SO_2 levels, would have triggered the global environmental change occurred on early Mars.

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