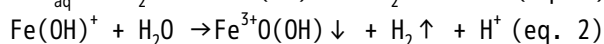
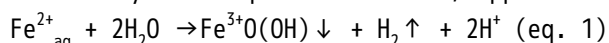


## Runaway acidification on early Mars triggered by atmospheric evolution

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Mineralogical and chemical observational data of sedimentary rocks deposited on early Mars suggest that chemistry of Mars' surface water had shifted from neutral pH (pH~7-9) to highly acidic (pH~2) at around 3.5 billion years ago (Ga) (Bibring et al., 2006; Ehlmann et al., 2011). One proposed mechanism for this acidification is photo-oxidation of ferrous iron dissolved in surface water (Hurowitz et al., 2010). When UV light is irradiated to surface water, ferrous iron are oxidized to ferric iron by producing H<sup>+</sup> with precipitation of Fe<sup>3+</sup> minerals (see Equations 1 and 2 below). Hurowitz et al. (2010) show that H<sup>+</sup> produced via this mechanism are quantitatively sufficient to explain the mineralogical and chemical compositions of sedimentary rocks in Meridiani Planum observed by Mars Exploration Rover, Opportunity (e.g., Tosca et al. 2005).



Although this mechanism would have promoted acidification at 3.5 Ga on Mars, it remains unsolved why surface water with neutral pH had been maintained before 3.5 Ga, and what the trigger for the acidification was. In this study, we propose a new hypothetical scenario to explain the chemical transition of surface water from neutral to acidic pH by considering positive and negative feedbacks in association with photo-oxidation of ferrous iron.

Ferrous iron has two stable dissolved species; Fe<sup>2+</sup> and Fe(OH)<sup>+</sup>, depending on pH of water. It has been reported that both species are oxidized when irradiated with UV (< 200 nm). But, Fe(OH)<sup>+</sup>, which becomes the dominant species at pH > 9, is also oxidized with irradiation of visible light (300-400 nm) (Braterman et al., 1983). In a thick CO<sub>2</sub> atmosphere (~1 bar) with several ppms of SO<sub>2</sub>, UV light with short wavelength (< 300 nm) is shielded by the atmospheric gas species. In this case, photo-oxidation of Fe(OH)<sup>+</sup> proceeds in surface water, whereas that of Fe<sup>2+</sup> is limited. In surface water with neutral to alkaline pH, photo-oxidation of Fe(OH)<sup>+</sup> acidifies the water forming H<sup>+</sup>. However, the concentration of Fe(OH)<sup>+</sup> drastically decreases around pH~6.5 via the conversion into Fe<sup>2+</sup>. This decrease in Fe(OH)<sup>+</sup> concentration, in turn, results in dampening Fe(OH)<sup>+</sup> photo-oxidation. Consequently, in a thick atmosphere, pH dependence of Fe(OH)<sup>+</sup> photo-oxidation works as a negative feedback to maintain surface water pH around neutral.

On the other hand, in a thin CO<sub>2</sub> atmosphere (0.1 bar or less) with < 1 ppm of SO<sub>2</sub>, UV light reaches to the surface water, leading to photo-oxidation of both Fe<sup>2+</sup> and Fe(OH)<sup>+</sup> in surface water. In this case, even if the concentration of Fe(OH)<sup>+</sup> in surface water decrease at pH~6.5, acidification proceeds via photo-oxidation of Fe<sup>2+</sup>. As a result, a runaway acidification to highly acidic surface water occurs via this positive feedback.

Here, we discuss the above possibility more quantitatively using the previous laboratory data on photo-oxidation rates of Fe<sup>2+</sup> under acidic conditions by Jortner et al. (1962) and those by Braterman et al. (1983) under neutral pH conditions. We calculate the total production rate of H<sup>+</sup> both via the photo-oxidation of Fe<sup>2+</sup> and Fe(OH)<sup>+</sup> for various atmospheric compositions and pressures. Based on our sensitivity study of the abundances of CO<sub>2</sub> and SO<sub>2</sub> to acidification of surface water, the critical atmospheric compositions to drive the runaway acidification are discussed.

Keywords: Mars, acidification, atmospheric evolution, photooxidation, geochemistry