

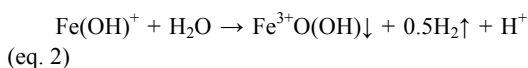
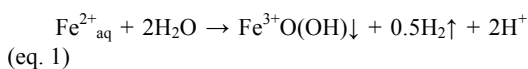
Effect of atmospheric evolution on surface acidification at Mars 3.5 Ga

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Chemical and mineralogical data on sedimentary rocks on Mars suggest that aqueous environments on early Mars had shifted from neutral (pH~7-9) to highly acidic pH (pH~2) at ~3.5 Ga (e.g., [1]). Using the observational data by Opportunity, the previous study shows that this surface acidification may have been driven by photo-oxidation of ferrous iron in surface water [2]. Irradiations of UV light photo-oxidizes ferrous iron to ferric iron in association with H⁺ production, as shown in the following equations.



Although this mechanism can explain the acidification, it remains unclear how neutral pH water had been sustained before 3.5 Ga and what was the trigger for the acidification.

Here we propose a hypothetical mechanism to address these questions by considering the dependence of these photo-oxidation processes on the atmospheric compositions. Ferrous iron exists in water as either Fe²⁺ (< pH~8) or Fe(OH)⁺ (> pH~8). While both ions are photo-oxidized upon UV irradiation (< 200 nm), Fe(OH)⁺ is also oxidized with irradiation of visible lights (300–400 nm) [3]. Thus, in a thick atmosphere with several ppm of SO₂, only Fe(OH)⁺ is photo-oxidized as UV is shielded. Under such conditions, surface water acidifies via the photo-oxidation of Fe(OH)⁺ (Eq. 2). Nevertheless, the acidification dampens in surface water at pH~7 because the concentration of Fe(OH)⁺ drastically decreases due to the conversion to Fe²⁺. This negative feedback mechanism can sustain pH circum-neutral. On the other hand, in an atmosphere with less SO₂, both Fe²⁺ and Fe(OH)⁺ are photo-oxidized as both UV and visible light reach to the surface. In such cases, the acidification continuously proceeds through Eq. 2 at neutral pH and through Eq. 1 at low pH. If the input flux of alkali ions into surface water is less than H⁺ production rate via the photo-oxidation, a runaway acidification occurs. Taking into account the experimental data [3][4], we here discuss the critical atmospheric compositions to trigger the runaway acidification.

- [1] Bibring *et al.* (2006) *Science* **312**, 400-404. [2] Hurowitz *et al.* (2010) *Nature Geosci.* **3**, 323-326. [3] Braterman *et al.* (1983) *Nature* **303**, 163-164. [4] Jortner *et al.* (1962) *J. Phys. Chem.* **66**, 1258-1264.