

EFFECT OF THE ATMOSPHERICALLY ATTENUATED SOLAR SPECTRUM AT THE SURFACE FOR ACIDIFICATION OF SURFACE WATER ON EARLY MARS. H. Tabata^{1,2}, Y. Sekine¹, Y. Kanzaki³, S. Sugita², ¹Earth-Life Sci. Inst., Tokyo Inst. Tech., ²Dept. Earth Planet. Sci., Univ. Tokyo, ³Dept. Earth Sci., U.C. Riverside.

Introduction: Many lines of both geological and geochemical evidence indicates that early Mars once possessed liquid water on the surface [1]. Global remote-sensing data of secondary minerals together with results of in-situ analyses for sedimentary rocks on Mars provide constraints on the aqueous environments on paleo-Mars [e.g., 1, 2].

One example of the observational constraints is evolution of surface water pH, which is estimated based on the secondary mineral assemblages of sedimentary rocks in outcrops observed by orbiters and rovers [2, 3]. The widespread occurrences of clay minerals, such as smectite, on Late Noachian and Early Hesperian (~4.0–3.5 Ga) terrains generally suggest circumneutral-pH surface water [1, 2], consistent with the prediction from thermochemical equilibrium calculations [4]. By contrast, sulfates and silica are locally observed on mid-Hesperian to Late Hesperian terrains (~3.5–3.0 Ga) [2]. The Opportunity rover landed on Meridiani Planum found deposits of Fe-sulfate (jarosite), which is estimated to have formed in mid-Hesperian and indicate the presence of acidic-pH water (pH 2–4) [3]. Although the occurrence of such highly acidic-pH water may have been only local [5], these results suggest that the pH of surface water may have shifted from circumneutral to acidic at around 3.5 Ga on early Mars [2].

A previous study has proposed that the ultraviolet (UV) photo-oxidation of dissolved ferrous ions may have acidified surface water: $2\text{Fe}^{2+} + 3\text{H}_2\text{O} + h\nu \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}^+ + \text{H}_2$ (or $2\text{FeOH}^+ + \text{H}_2\text{O} + h\nu \rightarrow \text{Fe}_2\text{O}_3 + 2\text{H}^+ + \text{H}_2$) [6]. Ferrous ions may have been supplied from upwelling groundwater [6]. However, both groundwater upwelling and solar light irradiation must have already occurred in Late Noachian/Early Hesperian. Thus, it is unclear why acidification occurred only in mid-Hesperian to Late Hesperian.

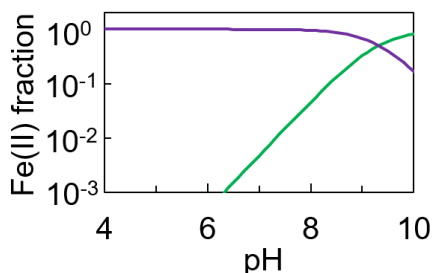


Figure 1: Chemical speciation of ferrous ion, Fe(II), as a function of pH. Purple line: Fe^{2+} and green line: FeOH^+ .

Here, we propose that the acidification of surface water on mid-Hesperian to Late Hesperian Mars may have been triggered by a change in the solar spectrum at the surface due to a change in the abundance and/or composition of the atmosphere. Ferrous ions have different chemical forms depending on pH (Fig. 1). In circumneutral-to-alkaline pH water, such as upwelling groundwater [4], FeOH^+ becomes a major form of ferrous ion as well as Fe^{2+} (Fig. 1). While Fe^{2+} is photo-oxidized only by UV light with wavelength < 300 nm, FeOH^+ can also be oxidized by photon in longer wavelength up to 450 nm [7]. Thus, if early Mars had an optically thick atmosphere that shielded the solar light with wavelength < 300 nm, only FeOH^+ would have been photo-oxidized at the surface. On the other hand, if early Mars had an optically thin atmosphere, both Fe^{2+} and FeOH^+ could have been photo-oxidized, possibly leading to efficient acidification of surface water.

In the present study, we investigate the effect of UV spectrum on the photo-oxidation of ferrous iron by laboratory experiments. Through the experiments, we examine the solution pHs and acidities achieved by photo-oxidation of ferrous ions under different irradiation spectra. To this end, dissolved O_2 in solutions is required to be down to ppb levels to prevent rapid oxidation at circumneutral pHs [8]. In our previous report [9], we performed experiments only at acidic pHs because we could deoxygenate solutions only down to ppm levels. Here, we report new results with sufficient deoxygenation (dissolved O_2 : ~1 ppb). Using the results, we compare the acidification mechanisms under different spectrum conditions. Finally, we discuss the atmospheric conditions capable of causing extreme acidification (pH 2–4) on Hesperian Mars.

Methods: We conducted experiments using a designed 500-ml cylindrical reaction vessel with a sampling port. The reaction vessel was made of quartz glass to ensure high UV transmittance at > 150 nm. The starting solutions of pH ~7 were prepared by mixing the solutions of 1 mM HNO_3 and 1 mM NaOH . Then, the solutions were deoxygenated via bubbling with pure Ar gas inside an Ar-purged glovebox ($p\text{O}_2 < 10^{-15}$ bar) until the dissolved oxygen of the solution reached less than ~1 ppb. Ferrous ion was added into the starting solution as $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ after the bubbling inside the glovebox. The initial concentration of total ferrous ion ($[\Sigma\text{Fe}^{2+}]_0 = [\text{Fe}^{2+}]_0 + [\text{FeOH}^+]_0$) was set to be 1 mM. Here, $[X]$ denotes the concentration of

species X and the suffix of “0” represents an initial state before the experiments

A 150-Watt Xe lamp was used as the light source as it provides a continuous emission spectrum from 200–800 nm, which is close to the solar spectrum. A colored-glass optical filter that cuts UV light with wavelength < 300 nm was set between the lamp and the vessel in the experiment to simulate an optically thick atmosphere. In the experiment to simulate an optically thin atmosphere, the solution in the vessel was irradiated with the Xe lamp without the optical filter. During the irradiation, ~2.5-ml sample solutions were collected several times in order to measure pH and $[\Sigma\text{Fe}^{2+}]$ in both of the experiments with and without the optical filter. Through the phenanthroline method, $[\Sigma\text{Fe}^{2+}]$ in the sample solutions were obtained using a UV-visible spectrometer.

Results: Figure 2 shows the time evolutions of pH and consumed $[\Sigma\text{Fe}^{2+}]$ during the experiments. When irradiated without the optical filter, the pH of the solution decreases down to ~4 (Fig. 2). This happens because $[\Sigma\text{Fe}^{2+}]$ continuously decreases owing to the UV irradiation without the optical filter. In the beginning of the experiment, both Fe^{2+} and FeOH^+ in the starting solution at pH ~7 are photo-oxidized by UV light at 200–450 nm, leading to a decrease in pH. Then, remaining FeOH^+ is converted into Fe^{2+} in the solution due to pH change (Fig. 1). Due to UV light at 200–300 nm, photo-oxidation of Fe^{2+} continues in the solution. Finally, a large part of the initial ferrous ion is converted into Fe(III), resulting in low pH.

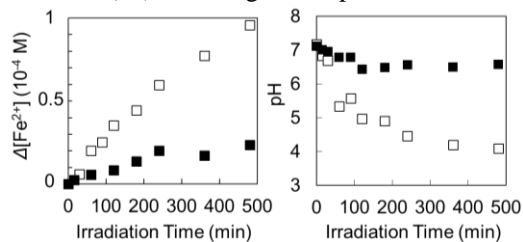


Figure 2: Time evolutions of pH and consumed $[\text{Fe}^{2+}]$ (or $\Delta[\Sigma\text{Fe}^{2+}]$). White and black squares: results without and with the optical filter, respectively.

In the experiment with the optical filter, in contrast, pH values stay around 7, although pH decreases slightly in the first 100 min of reaction time (Fig. 2). This is because photo-oxidation of Fe^{2+} is inhibited due to the lack of UV at 200–300 nm. In the beginning of the experiment, FeOH^+ is photo-oxidized by UV light at wavelengths 300–450 nm, causing a slight decrease in solution pH. A decrease in pH, in turn, converts remaining FeOH^+ to Fe^{2+} in the solution. However, photo-oxidation of Fe^{2+} occurs only by photon with wavelength < 300 nm. Thus, further photo-oxidation of Fe^{2+}

are dampened in the solution in the experiments using the optical filter, resulting in circumneutral pH even after a long time of the UV irradiation.

Discussion: Our results suggest that extremely low pH (e.g., pH 2–4) requires efficient photo-oxidation of Fe^{2+} on early Mars. This means that solar UV light with wavelength < 300 nm would have been required to reach the surface; that is, the Mars atmosphere had to be optically thin. In other words, if UV light is sufficiently shielded in an optically thick atmosphere, the effect of acidification due to photo-oxidation of ferrous ion would have been limited.

Candidates for the atmospheric gas species that absorb the UV light include CO_2 and SO_2 . Figure 3 shows calculated solar spectra at Mars' surface for various CO_2 - SO_2 atmospheres. This figure indicates that ≤ 1 bar of a pure CO_2 atmosphere is insufficient for shielding UV light with wavelength < 300 nm. On the other hand, trace amounts (e.g., 10^{-6} bar) of SO_2 in addition to a CO_2 atmosphere can efficiently shield UV light with wavelength < 300 nm (Fig. 3). A photochemical model suggests that 1 ppm of SO_2 in a 1-bar CO_2 atmosphere could have been achieved immediately after large-scale volcanic eruptions in Noachian to Early Hesperian [10]. As large-scale volcanic activity ceases in mid-Hesperian to Late Hesperian, solar UV light at < 300 nm would have reached the surface. This would have enabled extreme acidification of surface water possibly at local areas with groundwater upwelling.

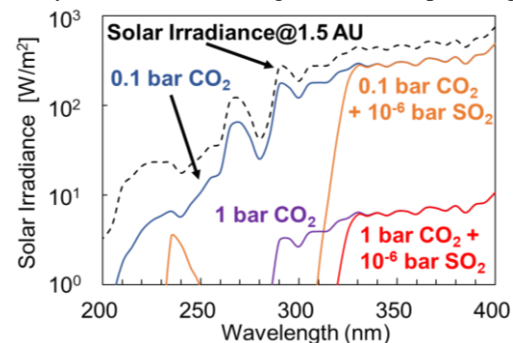


Figure 3: Calculated solar UV spectra at Martian surface with various CO_2 - SO_2 atmospheric compositions.

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