論文の内容の要旨

Photo-oxidation of ferrous iron: Implications for hydrogeochemistry of early lakes on Gale Crater, Mars

（二価鉄の光酸化：火星ゲイルクレータ古湖の水文地球化学への示唆）

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Lines of geological records obtained by Mars exploration suggest that Mars once had liquid water on its surface and that the water environment experienced acidification and oxidation about 3.5 billion years ago. Since the record of liquid water on the surface disappears at 3.5 billion years ago, revealing the acidification and the oxidation mechanism is important for understanding the evolution of the Martian surface. To reconstruct the early Martian hydrogeochemistry, in this thesis, I focused on the ferrous iron (Fe(II)) photo-oxidation mechanism.

When UV light of wavelength at < 300 nm is irradiated onto an aqueous solution containing dissolved Fe(II) salts, Fe^{2+} ions are photo-oxidized to ferric iron (Fe(III)) through producing H^+ via the following equation:

$$Fe^{2+} + 3H_2O \xrightarrow{h\nu} Fe(OH)_3 + 2H^+ + 0.5H_2.$$
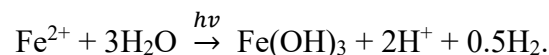
The reaction rate of the photochemical reaction is determined by experimentally measuring the quantum yield (i.e., the number of Fe(III) produced per the number of photons absorbed). However, previous studies have quantified the quantum yield of Fe(II) photo-oxidation only at pH < 3 due to the difficulty avoiding the oxidation by the dissolved O_2, which the reaction rate increases exponentially as pH increases. Since the

pH of the early Mars aqueous environment is estimated to be pH ~7, it was not possible to apply it for the Martian aqueous environment. Furthermore, at neutral pH, a fraction of the dissolved Fe(II) ion is converted to $FeOH^+$, which could absorb photons of wavelength at < 460 nm, and the quantum yield of $FeOH^+$ photo-oxidation has not been reported.

In Chapter 2 of this thesis, I performed a laboratory experiment of Fe(II) photo-oxidation utilizing an Ar-purged glovebox and a zirconia pump deoxygenating system, which could achieve low O_2 partial pressure of $< 10^{-15}$ bar. By preparing the pH buffer solution inside the glovebox, the quantum yields of Fe^{2+} photo-oxidation (φ_{Fe2+}) at pH of 2.0–7.6 was measured as follows:

$$\varphi_{Fe2+} = 0.103\ (\pm\ 0.005) + 2.17\ (\pm\ 0.27) \times [H^+]^{0.5}.$$

The quantum yield of $FeOH^+$ was also measured to be 0.08 ± 0.01 at pH 7.1–7.6 by adjusting the irradiation spectra of the light source to the wavelength of > 300 nm using an optical filter.

To evaluate the wavelength dependence of $FeOH^+$ photo-oxidation, experiments with the irradiation wavelength at > 200 nm, > 260 nm, and > 300 using optical filters against solutions without pH buffer were performed to investigate the timescale of acidification (Chapter 3). The quantum yields of $FeOH^+$ photo-oxidation were obtained from the initial reaction rate to be 0.13 ± 0.03 and 0.09 ± 0.01 for irradiation with a wavelength of > 260 nm and > 300 nm, respectively. The about 1.4 times higher quantum yield at irradiation of > 260 nm compared to > 300 nm suggests that although the quantum yield of $FeOH^+$ photo-oxidation shows a wavelength dependence, its variation is relatively small.

On the course of irradiation, while the solution pH drastically decreased to pH ~4 when irradiated with > 200 nm, it remained circum-neutral pH of ~6 for irradiations with > 260 nm and > 300 nm within the experimental time. Using the obtained reaction rate, the acidification timescale for Martian solar flux under various CO_2–SO_2 atmospheric compositions were calculated. It was found that although the reaction rate seems slow, $FeOH^+$ photo-oxidation would acidify the surface water pH to ~4 within a short timescale of $\sim 10^2$ years. Since various episodic warming mechanism has been proposed to sustain surface water for $> 10^2$ years, this result suggests the existence of a pH buffering mechanism on early Mars.

In order to constrain the geochemical conditions on Hesperian Mars, the reaction rates of Fe(II) photo-oxidation derived in Chapter 2 are applied to a reaction-transport model simulating the early Gale lake settings (Chapter 4). The appearances of oxidizing Fe oxides (e.g., hematite) in the coarser sediments and reducing Fe oxides (e.g., magnetite) in the finer sediments discovered by the Curiosity rover landed in the Gale Crater have led to a hypothesis that early Gale lakes could have been redox stratified. Fe(II) photo-oxidation could have created a vertical redox gradient because the oxidation tends to proceed near the surface due to an attenuation of solar photons. I constructed a one-dimensional geochemical model that aimed to investigate Fe(II) input fluxes, Fe(II) source (via rivers or groundwater), advection rate of the water column, pH of lake water, and atmospheric compositions to achieve redox stratification on early Gale lakes.

The results suggest that when Fe(II) is supplied via rivers, both acidic pH of 5 and a high Fe input flux are required for redox stratification. This is because dissolved Fe(II) supplied from the top layer needs to be transported to a deep part before Fe(II) photo-oxidization for redox stratification and because Fe(II) photo-oxidation rates are low at low pH. On the other hand, when Fe(II) is supplied via groundwater upwelling, redox stratification occurs in a wide range of parameters (pH 5–7) and moderate Fe input flux as long as the advection rate is kept small. High input fluxes of Fe(II) or CO_2 partial pressure of ~bar result in saturation with Fe(II)-carbonate, which is inconsistent with the in-situ observations detecting almost no carbonate minerals. Considering the recent estimate of the circum-neutral pH of early Gale lakes, these results prefer scenarios that Fe(II) was supplied via groundwater upwelling on paleo-Gale lakes. Required low advection rates imply that the depth of early Gale lakes would have been relatively deep (i.e., several hundred meters). Preferred low CO_2 in the atmosphere suggests a need for an abundance of other efficient greenhouse effect gases than CO_2 to warm the surface on early Mars.

A groundwater-supported aqueous environment on early Mars has been suggested in numerous locations based on geomorphological analyses. This thesis adds new hydrogeochemical constraints by combining laboratory experiments of Fe(II) photo-oxidation and hydrogeochemical model, utilizing the in-situ geochemical data obtained by the rover. A number of planned and ongoing planetary missions (e.g., Perseverance rover, ExoMars, MMX) are equipped with instruments capable of geochemical analyses. Therefore, the importance of understanding the fundamental geochemical processes in the planetary environments, as pursued in this thesis, is increasing.