Iron and oxygen isotope fractionation during iron UV photo-oxidation: Implications for early Earth and Mars

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Abstract

Banded iron formations (BIFs) contain appreciable amounts of ferric iron (Fe3+). The mechanism by which ferrous iron (Fe2+) was oxidized into Fe3+ in an atmosphere that was globally anoxic is highly debated. Of the three scenarios that have been proposed to explain BIF formation, photo-oxidation by UV photons is the only one that does not involve life (the other two are oxidation by O2 produced by photosynthesis, and anoxicogenic photosynthesis whereby Fe2+ is directly used as electron donor in place of water). We experimentally investigated iron and oxygen isotope fractionation imparted by iron photo-oxidation at a pH of 7.3. The iron isotope fractionation between precipitated Fe3+-bearing lepidocrocite and dissolved Fe2+ follows a Rayleigh distillation with an instantaneous 56Fe/54Fe fractionation factor of +1.2‰. Such enrichment in the heavy isotopes of iron is consistent with the values measured in BIFs. We also investigated the nature of the mass-fractionation law that governs iron isotope fractionation in the photo-oxidation experiments (i.e., the slope of the $^{56}\text{Fe}/^{54}\text{Fe}$ relationship). The experimental run products follow a mass-dependent law corresponding to the high-T equilibrium limit. The fact that a ~3.8 Gyr old BIF sample (IF-C) from Isua (Greenland) falls on the same fractionation line confirms that iron photo-oxidation in the surface layers of the oceans was a viable pathway to BIF formation in the Archean, when the atmosphere was largely transparent to UV photons.

Our experiments allow us to estimate the quantum yield of the photo-oxidation process (~0.07 iron atom oxidized per photon absorbed). This yield is used to model iron oxidation on early Mars. As the photo-oxidation proceeds, the aqueous medium becomes more acidic, which slows down the reaction by changing the speciation of iron to species that are less efficient at absorbing UV-photons. Iron photo-oxidation in centimeter to meter-deep water ponds would take months to years to complete. Oxidation by O2 in acidic conditions would be slower. Iron photo-oxidation is thus responsible for the formation of jarosite–hematite deposits on Mars, provided that shallow standing water bodies could persist for extended periods of time.

The oxygen isotopic composition of lepidocrocite precipitated from the photo-oxidation experiment was measured and it is related to the composition of water by mass-dependent fractionation. The precipitate-fluid $^{18}\text{O}/^{16}\text{O}$ isotope fractionation of ~+6‰ is consistent with previous determinations of oxygen equilibrium fraction factors between iron oxohydroxides and water.

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1. Introduction

Banded Iron Formations (BIFs) are chemical sedimentary rocks composed primarily of laminated iron-rich and silica-rich/iron-poor layers that are confined to the Precambrian, with most occurrences found in the Archean (James, 1954). The iron source is thought to have been predominantly marine hydrothermal ferrous iron Fe(II) (Bau et al., 1997; Dynek and Klein, 1988; Holland, 1973; Jacobsen and Pimentel-Klose, 1988; Klein, 2005), but continental contributions have also been identified (Alexander et al., 2009; Haugaa et al., 2013; Li et al., 2015; Miller and O’Nions, 1985; Viehmann et al., 2014; Wang et al., 2014). In the modern oxic ocean, the solubility and residence time of iron are low, but the globally anoxic conditions in the Archean allowed hydrothermal Fe(II) to be transported over wide distances until it was oxidized to less soluble ferric iron Fe(III), which precipitated to form BIFs. Despite decades of study, the nature of the oxidation mechanism responsible for BIF precipitation has remained elusive. Three sce-
narios have been proposed to account for Fe(II) oxidation in such an anoxic environment:

(1) In the photic zone, local “oxygen oases” could have been produced by the photosynthetic activity of cyanobacteria. Oxygen thus produced could have oxidized dissolved Fe(II) into insoluble Fe(III) that would have rapidly precipitated and sank to form layered deposits known as BIFs (Cloud, 1973, 1965). In the following, this is referred to as “O2-mediated oxidation”.

(2) A biogenic alternative to O2-mediated oxidation is anoxicogenic photosynthesis, whereby Fe(II) is used as the electron donor in place of water (e.g., Croal et al., 2004; Garrels et al., 1973; Hartman, 1984; Kappler et al., 2005; Widdel et al., 1993). In this scenario, carbon fixation and reduction from CO2 to organic carbon is coupled to intracelluar oxidation of Fe(II) into Fe(III).

(3) Without oxygen and ozone, the Archean atmosphere was largely transparent to UV photons that could reach the surface layers of the oceans. It was demonstrated experimentally that such UV could induce oxidation of Fe(II) into Fe(III) while releasing H2 in a process known as photo-oxidation (e.g., Braterman et al., 1983; Cairns-Smith, 1978). Among the three mechanisms considered for BIF formation, this is the only process that does not involve biology.

The viability of the abiological UV photo-oxidation for BIF formation was demonstrated by Braterman et al. (1983). Their experiments used an argon-flushed Fe(II)-containing solution illuminated by a medium-pressure mercury UV lamp. They found that the effective UV wavelength is pH dependent. At near-neutral pH (pH > 6.5), FeOH+ can efficiently absorb 300–450 nm UV light, leading to high Fe(II) oxidation rates. This chemical species, however, is not abundant at low pH (4.8–6.1) where 100–280 nm UV light induces the oxidation of dissolved Fe(II) to dissolved Fe(III). Anbar and Holland (1992) studied the photo-oxidation of manganese and found that Mn(II) oxidation was much less effective compared to that of Fe(II), and the Mn/Fe ratio of precipitates was consistent with field observations of Mn/Fe ratios in BIFs.

The main argument against photo-oxidation was laid out by Konhauser et al. (2007). They performed photo-oxidation experiments with Fe(II) solutions containing chemical species expected to be present in the Archean oceans (Si and Ca specifically). The experiments showed that most Fe(II) precipitated rapidly as Fe(II) silicate mineral greeneite and Fe(II) carbonate siderite, hindering Fe(II) photo-oxidation. Such mineral precipitation does not occur in oxidation pathways involving O2 or anoxicogenic Fe(II)-oxidizing bacteria. Given the uncertainties surrounding the influences of the young faint sun and weathering feedbacks on Earth’s climate in the Archean, it is not clear to what extent the temperature of 40°C and high pCO2-high dissolved silica concentrations used in the experiments of Konhauser et al. (2007) are representative of the conditions that prevailed in Earth’s oceans at that time.

In this work, we explore the possibility that photo-oxidation was involved in BIF formation by experimentally determining iron and oxygen isotope fractionation induced by this process and comparing the results with BIF signatures. Iron isotope fractionation between Fe(III) precipitate and dissolved Fe(II) in O2-mediated oxidation and in anoxicogenic photosynthesis has been measured previously (Bullen et al., 2001; Croal et al., 2004), and the two processes yield similar fractionation factors. However, the extent to which iron isotopes can be fractionated by photo-oxidation is still unknown. The only experiment on photo-oxidation-induced iron isotope fractionation was conducted at a very low pH of ~3 and yielded a fractionation between Fe(III) precipitate and dissolved Fe(II) of +2.5%, for the 56Fe/54Fe ratio (Staton et al., 2006). The results were only reported in abstract form and are not directly applicable to the near-neutral pH conditions that may have prevailed in the Archean ocean (between ~6.5 and 8 depending on the roles of high pCO2 and alteration of ultramafic rocks; Grotzinger and Kasting, 1993; Kempe and Degens, 1985; Morse and Mackenzie, 1998).

Photo-chemical reactions involving gaseous species of oxygen and sulfur are known to affect the isotopic compositions of those elements in ways that do not follow the rules of mass dependent fractionation (e.g., Chakraborty and Bhattacharya, 2003; Farquhar et al., 2001; Lyons, 2007; Thiemens and Heidenreich, 1983). Furthermore, even in systems that do exhibit mass-dependent behaviors, considerable information can be gleaned from a detailed investigation of the relevant mass-fractionation law, as different processes can produce distinct slopes in three-isotope diagrams (e.g., Dauphas and Schaeuble, 2016). Therefore, in addition to measuring the extent of O and Fe isotope fractionation, we also examine the mass-fractionation laws, or departure therefrom, imparted by iron photo-oxidation.

Photo-oxidation of iron has also been invoked to explain the formation of hematite on Mars (e.g., Burns, 1993; Burns and Fisher, 1993; Hurowitz et al., 2010; Lundgren et al., 1989; Schaefer, 1996). This hypothesis is also evaluated in light of our new results.

2. Methods

2.1. Experimental setup

The photo-oxidation reactions were conducted in an Ace Glass photo-chemical apparatus (Fig. 1). The main body consists of three parts: 1) a 450-Watt Hanovia medium pressure Hg lamp inserted into the center of an immersion well/reaction vessel to serve as a UV source. This lamp delivers a relatively broad and featureless spectrum between 220–1370 nm, and is a good proxy for solar light; 2) a quartz immersion well around the lamp connected to a chiller for cooling the system, and 3) a tightly sealed 500 ml borosilicate glass reaction vessel. The vessel has three ports that are used for Fe(II) injection, sampling, and temperature monitoring. UVs can be damaging to the eyes and generate toxic ozone, so the whole apparatus is placed in a non-reflective enclosure cabinet connected to an exhaust duct hose. The door of the cabinet has an automatic switch that turns off the UV light in case of inadvertent opening.

An air-tight Fe(II) injection section was designed to ensure that O2 plays no role in Fe(II) oxidation (Fig. 1). This section uses Ar-flushing lines, a syringe and a flask filled with Milli-Q water. The Fe(II) salt of (NH4)2Fe(SO4)2·6H2O in solid form is placed in the syringe. It is dissolved by deoxygenated water just before injection. The sampling section is placed in an Ar-filled glove bag to further avoid air infiltration. It consists of five sampling lines similar to the one depicted in Fig. 1. For each line, two syringes and one 0.1 μm Sartorius™ Minisart™ HF syringe filter are used. Two syringes are used to collect sample aliquots because Fe(III) precipitates tend to clog the filters, which makes it difficult to efficiently draw liquid. Pushing from one syringe to another allows one to apply more force. The detailed steps of an iron photo-oxidation experiment are shown in Fig. 1.

About 360 ml borate buffer solution was added to the reaction vessel to keep the reaction at a constant pH of ~7.3. Without the buffer, iron photo-oxidation would drive the solution to more acidic conditions through the reaction Fe2++ 2H2O → Fe(OH)↓ + 2H+ + 1/2H2↑↑, thereby changing the speciation of iron and the rate of iron oxidation. The buffer was made by adding 0.5 mol L−1 NaOH solution to 500 mL 0.6 mol L−1 H3BO3 solution to a final pH of 7.3. The H3BO3 solution was made by dissolving 18.55 g of solid H2BO3 in 500 mL Milli-Q water at room temperature. No pH change was observed during the experiments, consistent with the
prediction that the pH should decrease by about 0.2 units when all dissolved Fe(II) was oxidized.

High-purity argon gas (O₂ ≤ 1 ppm) was passed through the system to remove O₂. All the syringes were actuated several times to remove trapped O₂. After the system was deoxygenated, the Fe(II) salt was dissolved in the syringe by drawing some O₂-free water from the flask. Dissolved Fe(II) was then injected into the deoxygenated buffer solution in the reaction vessel and the UV lamp was turned on. A ferric iron precipitate started to form due to photo-oxidation of dissolved Fe(II). Several syringes in the sampling section were used to draw an aliquot of the liquid-precipitate mixture from the reaction vessel (a magnetic stirrer was used in the vessel to suspend the precipitate and homogenize the mixture) at regular intervals. The mixture was pushed through a filter into a second syringe. After filtration, the Fe(II)-bearing liquid was in the second syringe while the Fe(III) precipitate was on the filter. All dissolved Fe(II) in the filter was flushed by running deoxygenated Milli-Q water through it and recovering the flushed solution in a pre-cleaned centrifuge tube where it was combined with Fe(II) liquid from the second syringe. The Fe(III) precipitate was recovered from the filter in the glove bag by flushing the filter in the opposite direction with deoxygenated Milli-Q water.

In the course of the experiments, the temperature increased rapidly at the beginning (~1 °C/min) and stabilized to a steady value of ~45 °C after 20–30 min. Because oxygen isotopic analyses require more precipitate mass than Fe isotopic analyses, two distinct sets of experiments were undertaken: experiment #1 for Fe and experiment #2 for O. The initial concentration of Fe(II) was ~100 ppm or 1.8 mM, which is equivalent to the Fe concentration of some modern deep sea vents (Edmond et al., 1982) and surface water compositions modeled for the Burns Formation at Meridiani Planum on Mars (Tosca and McLennan, 2009). In experiment #1, 5 aliquots of ~7 mL each of the sample slurry mixture were sampled successively (the first one was sampled before turning on the UV lamp). In experiment #2, 6 aliquots of 18 mL each were sampled. The Fe(II) aliquot and a small fraction of the Fe(III) precipitate from experiment #1 were taken for iron isotopic analyses. The Fe(III) precipitate from experiment #2 was collected, rinsed with Milli-Q water and air dried in a fume hood overnight for oxygen isotopic analyses.
2.2. Purification and mass spectrometry

The chemical procedure for purifying Fe from unwanted elements (primarily Na and B from the borate buffer) is the one routinely used in our laboratory (Dauphas et al., 2004a, 2009; Dauphas and Rouxel, 2006). Iron concentration and isotope analyses were carried out on a Thermo Scientific Neptune MC-ICPMS at the University of Chicago. The extent of isotopic fractionation (δ-values) and departure from a reference mass-fractionation law (ε-values) were measured separately since they require different instrumental settings. δ-value analyses were performed using standard-bracketing method based on Dauphas et al. (2009). For ε-value measurements, solutions containing ~1 ppm Fe in 2% HNO₃ were introduced into the plasma torch with an Aridus II desolvating nebulizer without any auxiliary N₂. A 10¹⁰ Ω amplifier resistor was used for ⁵⁶Fe since the signal intensity was approximately 180 V with a combination of jet sampler and X skimmer cones (conventional 10¹¹ Ω amplifier resistors are limited to <50 V). The measurements were performed in high resolution mode, so that Ar⁺¹, Ar⁺², or ArOH⁺ peak tail interferences were kept to a minimum. Standard-bracketing was used to correct for instrumental fractionation, and the exponential law was used for calculating ε-values by fixing the ⁵⁷Fe/⁵⁶Fe ratio to 0.362549 (the ratio of IRMM-014). All iron isotope data are reported relative to the average isotopic composition of two bracketing standard solutions of IRMM-524, whose isotopic composition is identical to IRMM-014 (Craddock and Dauphas, 2011). The δ and ε values in units of per mil (‰) and per ten thousand are given by,

\[ \delta^i \text{Fe} = \frac{[\text{Fe}]}{[\text{Fe}]} \times 10^{3} \text{,} \]

\[ \epsilon^i \text{Fe} = \frac{[\text{Fe}]}{[\text{Fe}]} \times 10^{4} \text{,} \]

where \( i = 56, 57 \), or 58, and the star superscript indicates that the ratios were corrected for mass fractionation by internal normalization to a fixed ⁵⁷Fe/⁵⁶Fe ratio using the exponential law,

\[ \ln[\text{Fe}] / \text{Fe}]_{\text{sample}} = \ln[\text{Fe}] / \text{Fe}]_{\text{reference}} - \ln \left( \frac{\text{Fe} / \text{Fe}}{\text{Fe} / \text{Fe}} \right)_{\text{reference}} \times 10^{3} \text{,} \]

The bracketing standard is internally normalized to the same ⁵⁷Fe/⁵⁶Fe ratio using the exponential law. δ’ and ε’ notations are also used,

\[ \delta' \text{Fe} = \ln \left( \frac{\text{Fe}}{\text{Fe}} \right)_{\text{sample}} - \ln \left( \frac{\text{Fe}}{\text{Fe}} \right)_{\text{reference}} \times 10^{3} \text{,} \]

\[ \epsilon' \text{Fe} = \ln \left( \frac{\text{Fe}}{\text{Fe}} \right)_{\text{sample}} - \ln \left( \frac{\text{Fe}}{\text{Fe}} \right)_{\text{reference}} \times 10^{4} \text{.} \]

Oxygen isotopic compositions were measured at the Open University using the procedures outlined by Miller (1999). They are reported relative to the VSMOW standard (i = 17 or 18) as,

\[ \delta^i \text{O} = \ln \left( \frac{\text{O}}{\text{O}} \right)_{\text{sample}} / \ln \left( \frac{\text{O}}{\text{O}} \right)_{\text{VSMOW}} - 1 \times 10^{3} \text{,} \]

\[ \delta^i \text{O} = \ln \left( \frac{\text{O}}{\text{O}} \right)_{\text{sample}} / \ln \left( \frac{\text{O}}{\text{O}} \right)_{\text{VSMOW}} \times 10^{3} \text{,} \]

\[ \Delta^{17} \text{O} = \delta^{17} \text{O} - 0.5247 \times \delta^{18} \text{O} \text{.} \]

The value 0.5247 for the slope of the mass fractionation line in Eq. (8) is based on the data of Miller et al. (1999) and Miller (2002).

3. Results

Orange-colored particles formed upon irradiation. Orange-colored particles were observed in previous photo-oxidation experiments (Anbar and Holland, 1992; Braterman et al., 1983; Konhauser et al., 2007). XRD analyses indicate that those produced in our experiments were mainly lepidocrocite, with a small quantity of other Fe(III) oxides (see Appendix E), instead of amorphous two-line ferrihydrite seen previously (Konhauser et al., 2007). This difference in the nature of the precipitate may stem from differences in pH and silica contents between the two sets of experiments (Mayer and Jarrell, 1996; Schwertmann and Thalmann, 1976). Lepidocrocite is expected to precipitate near neutral pH (5–7) when Si/Fe ratio of the solution is lower than ~0.01 (our experimental conditions), whereas ferrihydrite would precipitate at a lower pH and a higher Si/Fe ratio (conditions in Konhauser et al., 2007). Even with active cooling (water surrounding the reaction vessel chilled to 5°C) and the lamp only inserted halfway, the temperature of the solution increased from ~20°C to ~45°C. Higher final temperatures of 60–90°C were achieved if the lamp was inserted more deeply. At these high temperatures, black-colored particles formed very rapidly, and the reaction reached completion in less than half an hour. These black particles were magnetite since they were attracted to a magnet; as was previously documented by Konhauser et al. (2007).

In control experiments below 50°C, when the UV lamp was switched off, no particles were produced. Above 50°C, a pale greenish colloid formed, which thermodynamic calculations show is most likely ferrous hydroxide Fe(OH)₂ (see Appendix F). Pure ferrous hydroxide is white in color and the greenish tint probably results from the presence of trace amounts of Fe(III), which could be due to oxidation by O₂ introduced as impurities in Ar gas. Upon exposure to air its color changed to orange within minutes, confirming that the colloid formed above 50°C contained mainly Fe(II).

The concentrations and isotopic compositions of iron are given in Table 1 [Fe(II)]ₐq is used hereafter to denote all dissolved Fe(II) species as iron(II) hexaquo is the main species predicted by Visual MINTEQ]. The [Fe(II)]ₐq concentration dropped from ~91 to 14 ppm after a 2-hr irradiation. The isotopic compositions of Fe(II)ₐq and Fe(III) precipitate evolved with time (Figs. 2, 3). Fe(II)ₐq had an
Table 1
Iron isotope fractionation in photo-oxidation experiment #1 and IF-G.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of Fe(II)aq (ppm)</th>
<th>Fraction of Fe precipitated</th>
<th>Illumination time (min)</th>
<th>δ(^{56})Fe ± 95% c.i. (‰)</th>
<th>δ(^{57})Fe ± 95% c.i. (‰)</th>
<th>δ(^{56})Fe ± 95% c.i. (‰)</th>
<th>δ(^{56})Fe ± 95% c.i. (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)aq</td>
<td>1</td>
<td></td>
<td>0</td>
<td>-0.311 ± 0.020</td>
<td>-0.471 ± 0.028</td>
<td>-0.632 ± 0.202</td>
<td>-0.009 ± 0.055</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>0</td>
<td>-1.050 ± 0.020</td>
<td>-1.548 ± 0.028</td>
<td>-2.153 ± 0.202</td>
<td>-0.114 ± 0.030</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>0</td>
<td>-1.580 ± 0.020</td>
<td>-2.430 ± 0.028</td>
<td>-3.330 ± 0.202</td>
<td>-0.150 ± 0.055</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>0</td>
<td>-2.138 ± 0.020</td>
<td>-3.153 ± 0.028</td>
<td>-4.226 ± 0.202</td>
<td>-0.218 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>0</td>
<td>-2.515 ± 0.020</td>
<td>-3.715 ± 0.028</td>
<td>-4.708 ± 0.202</td>
<td>-0.252 ± 0.030</td>
</tr>
<tr>
<td>Fe(III) precipitate</td>
<td>2</td>
<td></td>
<td>0</td>
<td>0.635 ± 0.027</td>
<td>0.922 ± 0.039</td>
<td>1.209 ± 0.248</td>
<td>0.042 ± 0.055</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>0</td>
<td>0.389 ± 0.027</td>
<td>0.579 ± 0.039</td>
<td>0.828 ± 0.248</td>
<td>0.001 ± 0.055</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>0</td>
<td>0.232 ± 0.027</td>
<td>0.352 ± 0.039</td>
<td>0.385 ± 0.248</td>
<td>0.025 ± 0.055</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>0</td>
<td>0.106 ± 0.027</td>
<td>0.162 ± 0.039</td>
<td>0.345 ± 0.248</td>
<td>0.017 ± 0.069</td>
</tr>
<tr>
<td>IF-G</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.611 ± 0.012</td>
<td>0.878 ± 0.019</td>
<td>1.172 ± 0.031</td>
<td>0.052 ± 0.030</td>
</tr>
</tbody>
</table>

δ-values are relative to standard IRMM-014, δ\(^{56}\)Fe values are internally normalized to δ\(^{57}\)Fe = -0.3625492 using the exponential law. δ\(^{56}\)Fe values are 95% confidence intervals. δ- and ε-values are as defined in Eq. (1) and Eq. (2). To convert δ- and ε-values to δ′- and ε′-values, the following equations are used: δ′ = 1000 × ln(δ/1000 + 1) and ε′ = 10000 × ln(ε/10000 + 1). n.a. = not applicable.

Fig. 3. Rayleigh fractionation behavior of the photo-oxidation samples. δ′ is calculated as ln (δ/1000 + 1), δ-values are from Table 1. Error bars are smaller than the symbols. The initial δ\(^{56}\)Fe value was subtracted from all the samples, so that the bulk mix solution-s-precipitate has a δ\(^{56}\)Fe value of 0. The iron precipitate corresponds to cumulative Fe(III). (a) The regression of Fe(II)aq samples yields an (α − 1) value of 0.00012 [δ\(^{56}\)Fe(III) precipitate – δ\(^{56}\)Fe(II)aq] = +1.2% at 45 °C. Distortion of green symbols corresponds to estimated errors. (b) The predicted curves for Rayleigh and batch equilibrium fractionations are shown as black and grey lines respectively. 1.0012 was used as the fractionation factor (α) in the Rayleigh distilled. For batch equilibrium fractionation trends, a fractionation of +1.2% between Fe(III) precipitate and Fe(II)aq was used. The formula described to use a Rayleigh process is δ\(^{56}\)Fe(III)aq = δ\(^{56}\)Fe(II)aq + ln(α/1000). Where δ\(^{56}\)Fe(II)aq is the isotopic composition of the reactant reservoir, subscript zero denotes the initial composition, f represents the fraction the reactant remains in the reactant reservoir, and α is the Rayleigh fractionation factor. If is calculated based on the concentration in the filtrated Fe(II)aq liquid in each aliquot, i.e., f = 1/C0, where C0 is the initial Fe(II)aq concentration. Plotting of δ\(^{56}\)Fe(III)aq/1000 vs. f yields a straight line with a slope of α − 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

initial δ\(^{56}\)Fe value of −0.31‰ relative to the IRMM-014 standard, and became enriched in the lighter isotopes as the reaction proceeded, reaching −2.5% in the last sampled aliquot. As expected based on mass balance, the δ\(^{56}\)Fe values of the Fe(III) precipitate were always heavier than Fe(II)aq but continuously decreased in response to the light isotope enrichment of the solution. The quantum yield of the reaction (iron atoms oxidized per photon absorbed) is ~0.07 (Appendix B), which is slightly higher than the value of ~0.01–0.05 inferred by Brateman et al. (1983).

A three-isotope plot of Fe(II)aq and Fe(III) precipitate yields a straight mass-dependent line with a slope of 0.677 for δ\(^{56}\)Fe vs. δ\(^{57}\)Fe (Fig. 2). No large mass-independent Fe isotope fractionation was observed. The most fractionated samples have small non-zero ε values, which is interpreted to reflect the fact that photo-oxidation follows a mass-fractionation law that differs from the exponential law that is used to correct for mass-dependent fractionation by internal normalization.

The results of experiment #2 dedicated to oxygen isotopic analyses are given in Table 2. The iron isotopic compositions follow the same temporal trend as in experiment #1. The oxygen isotopic composition of the Fe(III) precipitate (average +0.33%) is heavier than that of Chicago tap water used in the experiment, which is about −5.8‰ in terms of δ\(^{18}\)O (measured at the University of Chicago using a Gasbench II connected to a Delta V Isotope Ratio Mass Spectrometer). For comparison, air O2 has a δ\(^{18}\)O value of +23.5‰. Unlike Fe, where [Fe(II)aq] and Fe(III) precipitate evolved in the course of the photo-oxidation, no systematic trend of δ\(^{18}\)O with time was seen, consistent with the fact that the solution effectively acted as an infinite reservoir for oxygen. The Δ\(^{17}\)O values calculated from measured δ-values range between −0.133‰ and −0.048‰, with an average of −0.078‰, where the reference mass fractionation line is the terrestrial fractionation line with a slope of 0.5247 passing through VSMOW (Miller, 2002; Miller et al., 1999). The Δ\(^{17}\)O values are within the range expected for mass-dependent fractionation.

4. Discussion

Konhauser et al. (2007) found that Fe(II)aq tends to form insoluble amorphous precursor phases of Fe(II) minerals such as goethite and siderite once added to deoxygenated silica-rich and calcite-saturated solutions upon UV-exposure. If exposed to phototrophic bacteria or free O2, however, Fe(II)aq was oxidized very rapidly instead of precipitating as Fe(II)-bearing silicate or carbonate minerals. This was used as a circumstantial argument against photo-oxidation; implicating bacteria as a cause of BIF precipitation. However, several aspects of this study are worth
Table 2

Iron and oxygen isotope fractionation in photo-oxidation experiment #2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Illumination time (min)</th>
<th>Concentration of Fe(II)_{aq} (ppm)</th>
<th>Fraction of Fe precipitated</th>
<th>δ^{56}Fe ± 95% c.l. (%)</th>
<th>δ^{57}Fe ± 95% c.l. (%)</th>
<th>δ^{56}Fe ± 95% c.l. (%)</th>
<th>δ^{18}O ± 1SD (%)</th>
<th>δ^{17}O ± 1SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Fe(II)</td>
<td>0</td>
<td>76.9</td>
<td>0</td>
<td>−0.387 ± 0.038</td>
<td>−0.413 ± 0.053</td>
<td>−0.805 ± 0.330</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>2 Fe(II)</td>
<td>10</td>
<td>81.0</td>
<td>0</td>
<td>−0.316 ± 0.038</td>
<td>−0.460 ± 0.053</td>
<td>−0.777 ± 0.330</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>3 Fe(II)</td>
<td>30</td>
<td>67.4</td>
<td>0.15</td>
<td>−0.691 ± 0.038</td>
<td>−1.038 ± 0.053</td>
<td>−1.198 ± 0.330</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>4 Fe(II)</td>
<td>60</td>
<td>53.2</td>
<td>0.33</td>
<td>−0.840 ± 0.038</td>
<td>−1.240 ± 0.053</td>
<td>−1.747 ± 0.330</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>5 Fe(II)</td>
<td>120</td>
<td>53.4</td>
<td>0.32</td>
<td>−0.829 ± 0.038</td>
<td>−1.236 ± 0.053</td>
<td>−1.640 ± 0.330</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>6 Fe(II)</td>
<td>150</td>
<td>56.7</td>
<td>0.28</td>
<td>−0.868 ± 0.038</td>
<td>−1.258 ± 0.053</td>
<td>−1.622 ± 0.330</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>3 Fe(III)</td>
<td>30</td>
<td>n.a.</td>
<td>0.15</td>
<td>1.185 ± 0.044</td>
<td>1.744 ± 0.068</td>
<td>2.068 ± 0.629</td>
<td>−0.135 ± 0.209</td>
<td>−0.121 ± 0.106</td>
</tr>
<tr>
<td>4 Fe(III)</td>
<td>60</td>
<td>n.a.</td>
<td>0.33</td>
<td>0.924 ± 0.044</td>
<td>1.375 ± 0.068</td>
<td>1.634 ± 0.629</td>
<td>0.800 ± 0.209</td>
<td>0.372 ± 0.106</td>
</tr>
<tr>
<td>5 Fe(III)</td>
<td>120</td>
<td>n.a.</td>
<td>0.32</td>
<td>0.939 ± 0.044</td>
<td>1.392 ± 0.068</td>
<td>1.914 ± 0.629</td>
<td>0.746 ± 0.209</td>
<td>0.309 ± 0.106</td>
</tr>
<tr>
<td>6 Fe(III)</td>
<td>150</td>
<td>n.a.</td>
<td>0.28</td>
<td>0.952 ± 0.044</td>
<td>1.442 ± 0.068</td>
<td>2.207 ± 0.629</td>
<td>−0.096 ± 0.209</td>
<td>−0.183 ± 0.106</td>
</tr>
</tbody>
</table>

δ-values of iron and oxygen are relative to standards IRMM-014 and SMOW respectively. 95% c.l. are 95% confidence intervals. δ-values are as defined in Eq. (1) and Eq. (6). To convert δ-values to δ’-values, the following equation is used: δ′ = 1000 × ln(δ/1000 + 1). n.a. = not applicable.

further scrutiny. Firstly, the photo-oxidation efficiency of UV-A (315–400 nm) was negligible in their experiment, in contradiction with earlier studies indicating that light between 300–450 nm was effective at oxidizing iron when pH > 6.5 (Anbar and Holland, 1992; Braterman et al., 1983). Secondly, it is not clear how Fe(II)_{aq} would have remained dissolved and been carried over wide distances under the low solubility conditions examined by Konhauser et al. (2007) to form BIFs. Thirdly, in the photo-oxidation study of Konhauser et al. (2007), the pH decreased from near neutral to pH ~3.5 after approximately 0.1 mM Fe(II)_{aq} was oxidized. pH decrease is expected to slow down the photo-oxidation process significantly (Sect. 4.4; Braterman et al., 1983). Precambrian seawater was probably near neutral or slightly alkaline (Grotzinger and Kasting, 1993; Kempe and Degens, 1985; Morse and Mackenzie, 1998). Under such conditions, the rate of iron photo-oxidation is greatly enhanced by the presence of FeOH^{+} species. Therefore, the photo-oxidation rate in Konhauser et al. (2007) may have been underestimated.

Although difficult to determine accurately, the quantum yield of Fe(II)_{aq} oxidation [Fe(II) atoms oxidized per UV photon absorbed], is estimated to be ~0.07 (see Appendix B), in general agreement with, but slightly higher than, the value of 0.01–0.05 proposed by Braterman et al. (1983). With such a quantum yield, previous studies concluded that photo-oxidation was a viable pathway to BIF precipitation (Anbar and Holland, 1992; Braterman et al., 1983). In the following, we discuss the implications of our isotope results and quantum yield estimates for assessing the viability of the photo-oxidation process for BIF formation, and the possibility that hematite on Mars formed by photo-oxidation.

4.1. Iron isotope fractionation during photo-oxidation

The iron isotopic compositions of minerals in BIFs vary from −2.5 to +2.0‰, which covers almost the entire range encountered on Earth (Dauphas and Rouxel, 2006; Dauphas et al., 2016; Johnson et al., 2008). The heavy isotopic compositions are interpreted to reflect partial iron oxidation (Cradock and Dauphas, 2011; Dauphas et al., 2007, 2004b; Heimann et al., 2010; Johnson et al., 2008; Rouxel et al., 2005). It was indeed shown experimentally that partial oxidation of Fe(II)_{aq} into Fe(III) precipitate, either through anoxic photosynthesis (Balci et al., 2006; Croal et al., 2004) or O_{2}-mediated oxidation (Bullen et al., 2001; Welch et al., 2003) imparts a heavy isotopic composition to the Fe(III) precipitate. The low δ^{56}Fe values could be due to a variety of processes such as reservoir effects in dissolved Fe(II) (Rouxel et al., 2005) and postdepositional reworking by dissimilatory iron reduction (e.g., Cradock and Dauphas, 2011; Heimann et al., 2010; Johnson et al., 2008). Regardless of these complications, the first order observation that needs to be explained is the heavy isotope enrichment of BIFs.

The two microbial oxidation mechanisms of O_{2}-mediated and anoxic photosynthesis (Bullen et al., 2001; Croal et al., 2004) can explain the high δ^{56}Fe values measured in BIFs starting from a hydrothermal δ^{56}Fe value of ~−0.2‰. Bullen et al. (2001) measured iron isotope fractionation during O_{2}-mediated Fe(II)_{aq} oxidation at pH around 6 in a natural setting. They used a Rayleigh distillation model to derive a fractionation factor of +1.0% between ferrihydrite and Fe(II)_{aq} at room temperature. Croal et al. (2004) measured iron isotope fractionation during anoxic photosynthesis at pH around 7 and found that the poorly crystalline ferric oxide produced was enriched in heavier isotopes relative to Fe(II)_{aq} by +1.5 ± 0.2‰. Microbial Fe(II)_{aq} oxidation was also conducted at low pH (~3) (Balci et al., 2006) and the result is similar to the anoxic photosynthesis, with a fractionation factor of +2.2% between Fe(III)_{aq} and Fe(II)_{aq}, although such low pH conditions are probably irrelevant to Archean seawater.

The photo-oxidation experiments in this study were conducted at pH around 7.3. The iron isotope fractionation during the process can be reproduced by a Rayleigh distillation model with an instantaneous fractionation factor between Fe(III) precipitate and Fe(II)_{aq} of +1.2 ± 0.1‰ in δ^{56}Fe (Fig. 3). A batch equilibrium model fails to reproduce the data, demonstrating that there was no significant isotope exchange between precipitate and Fe(II)_{aq} after Fe(III) precipitation.

Equilibrium fractionation factors have been previously estimated for several pairs involving ferric oxide/oxyhydroxide, Fe(III)_{aq}, and Fe(II)_{aq} (Fig. 4). Those experiments were performed at different temperatures than the one used here, so we converted previous equilibrium fractionation factors to a temperature of 45 °C using Eq. (12) of Dauphas et al. (2012). Wu et al. (2011) determined experimentally the equilibrium fractionation factor between ferrihydrite and Fe(II)_{aq} corresponding to a value of ~+2.7% at 45 °C. Welch et al. (2003) studied the effect of temperature on the equilibrium fractionation factor between Fe(III)_{aq} and Fe(II)_{aq}. Combining their equation with the equilibrium fractionation factor measured by Skulan et al. (2002) for the system hematite–Fe(II)_{aq} at 98 °C yields a hematite–Fe(II)_{aq} equilibrium fractionation factor of +2.2% at 45 °C. All these values are significantly higher than the value documented here for Fe(III) precipitate produced by photo-oxidation vs. Fe(II)_{aq} (~+1.2‰). Beard et al. (2010) and Friedrich et al. (2014) measured a fractionation factor between goethite and Fe(II)_{aq} of ~+0.8‰ when extrapolated to 45 °C, which is more in line with the value reported here. This result, however, would imply that there is an equilibrium fractionation
of \( \sim +2\% \) between ferrihydrite and goethite (Wu et al. 2011; Beard et al. 2010; Friedrich et al. 2014), which is much larger than the +0.5\% fractionation predicted between ferrihydrite and hematite (Skulan et al. 2002; Welch et al. 2003; Wu et al. 2011). It is not clear what in the crystal chemistry of goethite would differentiate it so markedly from ferrihydrite and hematite. Independent nuclear resonant inelastic X-ray scattering (NRIXS) experiments on goethite (Blanchard et al. 2015) and ab initio calculations on Fe[II]aq (Rustad et al. 2010) support a larger fractionation between goethite and Fe[II]aq than the measured values. To summarize, the equilibrium fractionation factor between Fe[II]aq and lepidocrocite is unknown and existing data on iron oxides/oxyhydroxides are too uncertain to be of much guidance. The possibility that kinetic effects associated with precipitation may be present, as was documented previously in mineral precipitation experiments for hematite (Skulan et al. 2002), siderite (Wiesli et al. 2004) and FeS (Butler et al. 2005), also confounds interpretations.

The instantaneous fractionation factor between Fe[III] precipitate and Fe[II]aq given by our experiments is lower than the one obtained in the photo-oxidation experiment of Staton et al. (2006), which may be due to differences in photo-oxidation mechanisms and iron speciation under acidic conditions. This value is, however, similar to the fractionation values in anoxic photosynthetic oxidation of Fe[II]aq (+1.5\%; Croal et al. 2004) and in O$_2$-mediated oxidation \( \sim +1\% \); Bullen et al. 2001). This demonstrates that, like the other two oxidation processes, photo-oxidation can also explain the heavy \( 56^{\text{Fe}} \) values measured in BIFs. Therefore, the three processes are not distinguishable based on the extent of iron isotope fractionation alone.

### 4.2. Mass-dependent fractionation law for photo-oxidation

Since the extent of iron isotope fractionation shown by the three oxidation scenarios is similar, another way in which these processes might be distinguished is to examine the mass-dependent fractionation laws that govern isotopic variations. In the experiments, no large mass-independent effects were observed that could be used to exclude photo-oxidation as a pathway to BIF precipitation. Terrestrial mass-independent Fe isotope fractionation has only been documented once in magnetite produced by magnetotactic bacteria (Amor et al. 2016), but the process is probably irrelevant to BIF formation since BIFs show only mass-dependent effects.

Beyond mass-independent effects, the mass-dependence of the isotope fractionation can also provide insights into natural processes (Dauphas and Schauble 2016 and references therein). Indeed, different processes can impart slightly different slopes in a 3-isotope diagram (e.g., O: Angert et al. 2003; Levin et al. 2014; Luz and Barkan 2010; Matsuhisa et al. 1978; Miller 2002; Pack and Herwartz 2014; Young et al. 2002; S. Farquhar et al. 2001; Mg: Young et al. 2012; Ca and Ti: Zhang et al. 2014). The slope \( \theta \) in a 3-isotope diagram is given by,

\[
\theta^{i1,i2,i3} = \frac{\delta^{i1}/i1}{\delta^{i3}/i3} = \frac{\ln(R^{i2}/i2/R^{i1}/i1)}{\ln(R^{i3}/i3/R^{i1}/i1)},
\]

which can be parameterized as,

\[
\theta^{i1,i2,i3} = \frac{m_i^n - m_i}{m_i^n - m_i^0},
\]

where \( m \) is the mass of an isotopic species. Different mass-fractionation laws define different slopes characterized by different values of \( n \) (Dauphas and Schauble 2016). The most commonly encountered law corresponds to equilibrium fractionation between coexisting phases in the high temperature limit, which gives \( n = -1 \). The limit \( n \to 0 \) corresponds to the exponential law commonly encountered in mass spectrometry and used in the present study to correct the measurements for instrumental mass fractionation. The laws given above describe mass fractionation when a single process is involved. In our case, this corresponds to the instantaneous fractionation of iron between the first Fe[III] precipitate removed and dissolved Fe[II]aq,

\[
\theta_{\text{inst}} = \frac{\delta^{57}_{\text{Fe}}(\text{III})_{\text{ppt}} - \delta^{56}_{\text{Fe}}(\text{II})_{\text{aq}}}{\delta^{57}_{\text{Fe}}(\text{III})_{\text{ppt}} - \delta^{56}_{\text{Fe}}(\text{II})_{\text{aq}}},
\]

This instantaneous fractionation is incorporated in a Rayleigh distillation, and what we are interested in is the effective mass fractionation slope \( \theta_{\text{eff}} \) (or apparent \( \theta \)) of the Rayleigh process for a given \( \theta_{\text{inst}} \). In a Rayleigh distillation, \( \theta_{\text{eff}} \) of the reactant [Fe[II]aq] and product [Fe[III] precipitate] differ from each other and from \( \theta_{\text{inst}} \). To first order, however, one can safely use the approximation \( \theta_{\text{solution}} \sim \theta_{\text{eff}} \) precipitate \( \sim \theta_{\text{inst}} \) (see Appendix A). To facilitate visualization of mass-fractionation laws, isotopic compositions are recast as departures from a reference mass-fractionation law (exponential law) used to correct isotopic ratios through internal normalization (Eq. (3)). Different laws are represented by different lines characterized by different \( n \) values in \( \epsilon' \) vs. \( \delta' \) diagram (Fig. 5a),

\[
\epsilon'^{i1,i2,i3} = 10 \left( \frac{m_i^n - m_i}{m_i^n - m_i^0} \ln(m_i/n) \right) \delta'^{i1,i2,i3}.
\]
Fig. 5. Iron mass-fractionation law associated with photo-oxidation. δ′ and ε′ are calculated as ln ( δ/1000 + 1) and ln ( δ/1000 + 1), respectively, and δ- and ε-values are from Table 1. Samples from the photo-oxidation experiment are plotted as green dots for Fe(II)aq and orange squares for Fe(III) precipitate. The 3.8 Gyr old BIF IF-G is plotted as a black hexagon. (a) The photo-oxidation reaction follows the equilibrium isotope fractionation law (n = -1) within error, so does the BIF sample IF-G. Different lines represent different mass fractionation laws; they are all expressed relative to the exponential law since the measured εδFe values are internally normalized to a fixed δ57Fe/δ56Fe ratio using the exponential law. θ is the corresponding slope in the 3-isotope diagram, it is related to n by Eq. (10). The δ′- and ε′-values have all had the starting isotopic composition subtracted. (b) A linear regression of the samples (the black line) gives a slope of +0.0652 ± 0.0087, which corresponds to n = -1.05 ± 0.14 using Eq. (14). Dashed red lines indicate the 95% confidence interval of the regression. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

\[
\varepsilon'_{\text{12/11}} \approx 5(n - k) \left( \frac{m_{12} - m_{11}}{m_{11}} \right) \text{F},
\]

where F is the degree of isotopic fractionation in \%/amu; k = 0 for exponential law. Applying this equation to the \(^{56}\text{Fe}^{54}\text{Fe}\) ratio (m_{12} = m_{sFe}, m_{2} = m_{sFe}, m_{13} = m_{sFe}, \delta^{57}\text{Fe} = (m_{38Fe} - m_{34Fe}) \text{F}),

\[
\varepsilon^{56}\text{Fe} = -0.062 \times n \times \delta^{57}\text{Fe}.
\]

The samples define a slope of 0.0652 ± 0.0087 (Fig. 5b), which corresponds to n = -1.05 ± 0.14 using Eq. (14). Within error, the samples fall on the high-temperature limit equilibrium-law line (n = -1). However, this does not necessarily imply that the instantaneous Fe(III) precipitate is in equilibrium with Fe(II)aq as it is conceivable that some kinetic processes would display the same mass-dependent exponent as the equilibrium law.

A ~3.7–3.8 Gyr old iron formation from Isua, Greenland was also measured (geostandard IF-G, Table 1 and Fig. 5a). It is well suited to compare with the experiments because it has a heavy iron isotopic composition relative to most BIFs (\delta^{57}\text{Fe} = +0.88\%), thus providing more leverage to distinguish between mass fractionation laws. The isotopic composition of IF-G agrees with the n = -1 law obtained for photo-oxidation.

Although the fractionation is large compared to variations encountered in other natural systems, the maximum iron isotope fractionation expected in BIFs (the products of iron oxidation) is the instantaneous precipitated Fe(III)-dissolved Fe(II) fractionation factor. In a Rayleigh distillation, much larger fractionation is expected in the source reservoir, that is, the seawater remaining after BIF precipitation. Rouxel et al. (2005) measured the Fe isotopic compositions of sulfides from shales of various ages and found large variations, which they interpreted to result from BIF precipitation and the impact that it has on the Fe isotopic composition of seawater. This interpretation was questioned (Archer and Vance, 2006; Yamaguchi and Ohmoto, 2006), but if correct, high precision Fe isotopic analyses of sulfides in shales could help better constrain the nature of the mass fractionation law associated with BIF formation. The Fe isotopic composition of shales has been extensively studied but the measurements are of insufficient precision to examine the nature of the mass fractionation law.

Adopt high-precision data is also missing for O2-mediated oxidation and anoxygenic photosynthesis, which is needed to compare with the photo-oxidation presented here. It may be expected, however, that O2-mediated oxidation in a regime where kinetic isotope effects are limited (at low oxidation rate) would also follow the equilibrium law discussed above, in which case it would be impossible to distinguish between the various oxidation mechanisms that have been proposed to explain the formation of BIFs. Regardless of these complications, this study demonstrates that photo-oxidation remains a viable option for explaining the precipitation of BIFs.

4.3. Oxygen isotope fractionation in photo-oxidation

The isotopic composition of oxygen was measured to explore whether photo-oxidation by UV light could produce anomalous effects. It is now well established that gas photochemistry can impart mass-independent fractionation for some species of oxygen and sulfur (e.g., Chakraborty and Bhattacharya, 2003; Farquhar et al., 2001; Lyons, 2007; Thiemens and Heidenreich, 1983). UV light can cause photolysis of gaseous O2 to form ozone which will be enriched in mass-independent heavier oxygen isotopes of \(^{17}\text{O}\) and \(^{18}\text{O}\) (Heidenreich and Thiemens, 1983; Thiemens and Jackson, 1987). UV photochemistry has also been implicated in creating the pervasive oxygen isotope anomalies documented in planetary materials, including meteorites, the favored mechanism being self-shielding associated with CO photo-dissociation (Clayton, 2002; Lyons and Young, 2005; Yurimoto and Kuramoto, 2004). To our knowledge, there is as yet no known aqueous process that results in mass-independent oxygen isotope fractionation.

In our experiments we did not detect any mass-independent isotope effects for oxygen in the Fe(III) precipitate produced by photo-oxidation. This could either be because photo-oxidation does not induce mass-independent fractionation in oxygen, or alternatively the Fe(III) precipitate equilibrated with atmospheric oxygen or pore water during drying, thus erasing the mass-independent signature. The issue of oxygen isotopic exchange between ferric oxyhydroxides and water upon drying is a known problem in experiments aimed at characterizing equilibrium fractionation factors and may be responsible for discrepancies between published values (Bao and Koch, 1999 and references therein). It is exacerbated when amorphous ferric gels and poorly crystalline phases are present that can exchange with non-structural water when they transform into stable ferric oxide phases upon drying. Our experiments were performed at relatively high temperature (45 °C) and most likely the Fe(III) precipitate lepidocrocite produced is relatively stable and not prone to exchange by air-drying at room
temperature. Non-structural water was further removed under vacuum prior to fluorination and isotopic analysis. We take the measured oxygen isotopic composition of the solid as representative of the primary precipitate, but further work is needed to unambiguously confirm this.

Overall, the iron precipitates show δ18O values with little dispersion, ranging from −0.14 to +0.80‰, with an average of ~+0.33‰. The isotopic composition of the starting water was ~5.8‰, similar to the δ18O value of lake Michigan (Bowen et al., 2007). There is thus a ~+6‰ fractionation between Fe(III) precipitate and water. This fractionation at ~45°C is consistent with the limited equilibrium fractionation documented in previous experiments between ferric oxides and water (Fig. 6). Previous experimental determinations show that equilibrium oxygen isotope fractionation factors of goethite, hematite and akaganeite are similar, varying between ~−2 and +4‰, at 45°C depending on the synthesis protocol and drying procedure involved, but all are centered around zero (Bao and Koch, 1999; Friedrich et al., 2015; Yapp, 2007). The photo-oxidation oxygen isotopes thus seem to record equilibrium isotope fractionation between the precipitate and surrounding water. In the context of BIF genesis, structural oxygen would have exchanged with surrounding pore water and oxygen-bearing phases during diagenesis and maturation to make magnetite and hematite, so comparison with the rock record is not straightforward.

4.4. Hematite formation on Mars through photo-oxidation

In addition to BIF precipitation, photo-oxidation may also be relevant to the formation of hematite on early Mars. Gray hematite was identified remotely on the Martian surface in Sinus Meridiani, Aram Chaos and numerous scattered locations by Mars Global Surveyor (Christensen et al., 2001). The presence of gray hematite was confirmed by NASA’s Opportunity rover that landed in Meridiani Planum in 2004 (Klingelhöfer et al., 2004). Hematite is hosted in layered sedimentary rocks, which have a thickness of several hundred meters and cover a surface area exceeding 105 square kilometers (Arvidson et al., 2006; Hynek and Phillips, 2008). Sulfate minerals such as Mg-, Ca-, and Fe3+-bearing jarosite coexist with hematite. This mineral assemblage is best explained by chemical precipitation through evaporation of water produced by acid-sulfate alteration of basaltic rocks followed by diagenetic alteration through interaction with groundwater (Klingelhöfer et al., 2004; McLennan et al., 2005; Tosca et al., 2005). The geologic setting for these deposits is thought to be reworked dry aeolian dune and wet interdune-playa deposits formed in an arid environment with a fluctuating water table (Grotzinger et al., 2005). These sulfate-rich deposits are of late Noachian to early Hesperian age (~3.8–3.5 Ga), corresponding to a time in the Martian history when the climate was thought to have been relatively arid. In such an environment, water ponds would have been ephemeral (Grotzinger et al., 2005). Interestingly, recent in-situ observations by the Curiosity rover of ca. 3.8–3.1 Ga sedimentary deposits in Gale Crater indicate the persistence of a long-lived lake environment (Grotzinger et al., 2015), which suggests a very different climate than that implied by the evaporite deposits at Meridiani Planum. This contrast suggests that the climate record from late Noachian to early Hesperian sedimentary rocks may be more local to regional than global in character. Remote observations also support the existence of paleolakes several hundred meters deep that could have persisted for hundreds to thousands of years or longer (e.g., Dehouck et al., 2010; Ehlmann et al., 2008; Grant et al., 2008; Wray et al., 2011). Those lakes contain phyllosilicate deposits and are mostly of Noachian age (~4.1–3.7 Ga), a period when the Martian climate was relatively warm and wet.

Iron in Martian basalts is present in its reduced form, Fe2+. One possibility to explain the presence of ferric iron in hematite–sulfate deposits is that iron was photo-oxidized by UV photons (Hurowitz et al., 2010) in a similar manner to the mechanism proposed for BIF formation. One important difference, however, is that while in the case of the early Earth the pH was probably close to neutral, deposition of jarosite suggests that the Martian conditions would have been acidic and so have affected the efficiency with which iron was oxidized. Hurowitz et al. (2010) gave a first order estimate of the photo-oxidation rate at 1cm and 1m water depths based on the rates found in early photo-oxidation experiments (Jortner and Stein, 1962), but they did not take into account the slowing of photo-oxidation as the water body evolved. We have developed a model (see Appendix C) to more realistically simulate the process of photo-oxidation on Mars using our new estimate of the quantum yield (iron atoms oxidized per photon absorbed) for photo-oxidation. We use our model to estimate the timescale needed for a water body containing Fe(II) to be oxidized. The initial pH of the water body is set at 7 and then decreases as Fe(II) is oxidized and H+ ions are produced. The ions in solution are Na+, K+, Fe2+, Mg2+, Ca2+, SO42−, Cl−, FeOH+ from Fe2+ hydrolysis, and FeCl+. The initial concentrations of Fe2+, SO42−, Cl− are from Tosca and McLennan (2009). The model used here is a closed system, meaning that it does not take into consideration the buffering capacity and replenishment of ions from water–rock interaction.

The rate of Fe(II) photo-oxidation decreases quickly (Appendix C) as the reaction proceeds because the Fe(II)aq concentration decreases and the pH decreases (less FeOH+ is present and UV-photon are less efficiently absorbed). The timescales for Fe(II) oxidation are shown in Fig. 7 for five different depths (1, 10 cm, 1, 10, and 100 m). For very shallow water bodies most relevant to playa-type deposits, the rate of Fe(II) oxidation is high at the beginning but decreases rapidly as the pH decreases. For 1 cm water depth, 50% iron oxidation can happen on a timescale of ~50 days, while 95% iron oxidation would take ~200 days. For 1 m depth, the timescales become ~400 days and ~900 days, respectively (Fig. 7). These timescales are considerably longer than the 1–50 days obtained in the model of Hurowitz et al. (2010), which does not take into account pH changes during photo-oxidation, changes in the intensity and spectrum of solar UV, solar incident angle, the greater distance of Mars from the Sun than Earth, and the diurnal effect (i.e., photo-oxidation only works during daytime). Despite these differences, our new results confirm that photo-oxidation is
Fig. 7. Elemental concentration and pH evolution of water bodies with different water depths exposed to UV at the surface of Mars (see text and appendix for details). The initial pH is 7. For 1 cm and 1 m depth, it takes ~200 and 900 days to oxidize 95% of Fe(II)aq respectively, much longer than the 1–50 days obtained in Hurowitz et al. (2010).
a viable mechanism to explain jarosite–hematite occurrences on Mars provided that shallow water bodies could persist for periods of months to years. For deeper and more persistent water bodies, an additional complication is ice coverage, which would significantly increase the timescales needed to complete photo-oxidation (Fig. 8).

At low pH, oxidation of iron by O$_2$ is considerably slower than photo-oxidation, with timescales up to hundreds of thousands of years in conditions relevant to early Mars (Hurowitz et al., 2010; Fig. 9; Appendix D). Unlike photo-oxidation, however, oxidation by O$_2$ does not require waters to be exposed to sunlight, so the process can occur in ground water. A difficulty with that scenario is that water–rock interactions would keep the pH near neutral, inhibiting the transport of Fe(II)$_{eq}$ and the formation of jarosite. One possible mechanism that could promote Fe(II)$_{eq}$ transport, described in Balridge et al. (2009) and Hurowitz et al. (2010), is for iron transport to take place in anoxic, circum-neutral pH groundwater, followed by O$_2$-mediated oxidation upon groundwater emergence in the shallow subsurface. On Earth, Fe(II) oxidation by O$_2$ in low pH environments such as acid mine drainage is largely mediated by bacteria that use iron oxidation as an energy source (Nordstrom and Southam, 1997). Another possibility would therefore be that the oxidation of Fe(II) by O$_2$ on early Mars involved biological activity. Despite the good preservation and availability of terrestrial BIFs, the involvement of life in their precipitation and diageneis is very much debated. The difficulty may stem from the fact that bacteria can respire organics using ferric iron as an electron acceptor in a process known as dissimilatory iron reduction, so that organic carbon was mineralized after deposition. If life was ever present on Mars and microbial ecosystems shared any similarity with terrestrial ones, detecting it in hematite–jarosite deposits may prove to be difficult, except possibly by examining stable isotope biosignatures. Unless evidence for life on Mars is found, photo-oxidation in bodies of standing water is a very likely pathway to form jarosite–hematite deposits on Mars.

5. Conclusion

Experiments of Fe(II) photo-oxidation by UV light were performed to measure iron and oxygen isotope fractionation associated with this process and to test whether it is a viable mechanism for BIF formation and iron oxidation on early Mars. The precipitate and solution show a Rayleigh fractionation relationship associated with an instantaneous fractionation factor of $+1.2 \pm 0.1\%$ for the $^{56}$Fe/$^{54}$Fe ratio (Fig. 3). This value is comparable to previously documented isotope fractionation factors for O$_2$-mediated oxidation and anoxicogenic photosynthesis, the two biogenic alternatives for BIF formation. High-precision iron isotopic analyses show that the mass fractionation law for photo-oxidation is the equilibrium high-temperature limit ($n = -1$; Fig. 5). IF-G, the only banded-iron-formation measured for iron isotopes at high precision has an isotopic composition that falls on the same law (Fig. 5). Our results show that photo-oxidation remains a viable pathway to BIF formation.

The oxygen isotopic composition of Fe(III) precipitate formed by photo-oxidation of Fe(II) yields a $\delta^{18}O$ fractionation between the two of $+6\%$ at 45°C (Fig. 6). This is consistent with previous experiments of equilibrium fractionation between Fe(III) oxihydroxides and water. No mass-independent effect is observed for oxygen.

Using our new estimate of the quantum yield for the iron photo-oxidation reaction, the timescale for Fe(II) photo-oxidation on Mars has been calculated (Fig. 7), and compared to that of the oxidation by O$_2$ (Fig. 9). It shows that photo-oxidation is a very likely pathway to form hematite–jarosite deposits on early Mars provided that shallow water bodies persisted for months to years. In acidic conditions, the kinetics of iron oxidation by O$_2$ are even longer, unless this was mediated by some form of biological activity, which has not yet been detected.

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Appendix. Supplementary material

Supplementary material related to this article can be found on

line at http://dx.doi.org/10.1016/j.epsl.2016.10.035.

References


