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Abiotic anoxic iron oxidation, formation of Archean banded iron formations, and the oxidation of early Earth



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ABSTRACT

Iron in the early anoxic oceans of Archean age (4000-2500 million years ago) is believed to have been oxidized to form banded iron formations (BIF). Previously, it has been proposed that iron was oxidized either by free oxygen, H₂O₂, microbial oxidation, or photo-oxidation. However, these mechanisms are difficult to reconcile with evidence for the oceans at that time having been largely devoid of dissolved oxygen and oxidants, together with the rarity of microbial remains in BIF and restrictively slow rates of photo-oxidation. Experiments reported here show that ferrous iron readily oxidizes in analogs of Archean anoxic seawater following the precipitation of ferrous hydroxide. Once precipitated, ferrous hydroxide undergoes decomposition to elemental iron that reacts with water at room temperature to form ferric iron and release hydrogen gas. The ferric iron may then be incorporated into green rust, a mixed ferrousferric phase that ages into iron minerals commonly found in BIF. Our finding suggests that anoxic iron oxidation may have contributed to the formation of oxide-facies BIF, especially Algoma-type BIF that likely formed in semi-restricted basins where ferrous hydroxide saturation was more easily achieved. Additionally, ferrous hydroxide decomposition would have contributed to early Earth's oxidation, as a result of hydrogen escape to space, thus providing new insights into environmental and biological conditions on early Earth.

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1. Introduction

Massive episodic deposition of banded iron formations (BIF), generally containing magnetite ($Fe_2^{2+}Fe_2^{3+}O_4$), hematite ($Fe_2^{3+}O_3$),

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https://doi.org/10.1016/j.epsl.2022.117469 0012-821X/ $\ensuremath{\mathbb{C}}$ 2022 Elsevier B.V. All rights reserved. and quartz (SiO₂) in Precambrian oceans (>543 Ma) has important implications for the earliest lifeforms and environmental conditions on early Earth (Konhauser et al., 2017). In the Archean period (4000-2500 Ma), BIF were deposited within marine sediments on stable continental margins (Superior-type) and also in association with volcanic rocks and many volcanogenic massive sulfide deposits (Algoma-type) (Bekker et al., 2010; Konhauser et al., 2017). The laminated appearance of BIF deposits has been attributed to deposition in deep water below wave base, in contrast

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to granular iron formations that lack banding and contain ooids and granules of iron oxide and chert, thus recording shallow water deposition (Bekker et al., 2010; Klein, 2005). The variable sedimentological and mineralogical compositions of BIF have long been used for further subdivision into silicate, oxide, and carbonate facies (James, 1954). These different BIF types suggest that their depositional mechanisms varied widely and reflect a range of environments across varying oceanic depths with variable degrees of diagenetic processing of iron dependant on the supply of organic matter (Bekker et al., 2010; Klein, 2005; Konhauser et al., 2017). Major BIF depositional periods occurred at ca. 2960 Ma and from ca. 2750 to ca. 2500 Ma; the oldest known BIF, more than 3,700 Ma, are found in the Isua, Nuvvuagittuq, and Saglek supracrustal belts (Bekker et al., 2010; Konhauser et al., 2017). It is generally accepted that Precambrian BIF sourced iron from the hydrothermal alteration of mafic rocks beneath the seafloor (Isley, 1995; Jacobsen and Pimentel-Klose, 1988; Li et al., 2015). However, in some BIF, coupled trends in Nd and Fe isotopes have been taken as evidence for a dissimilatory iron reduction shuttle of continentally derived iron to the oceans in which BIF were forming (Li et al., 2015). When this iron is released during such alteration, it enters into seawater as dissolved ferrous iron; the majority is believed to have been transported onto continental margins and then oxidized to ferric iron that precipitated to form Superior-type BIF (Sun et al., 2015). In contrast, several other studies have proposed that ferric iron in BIF is largely derived from the secondary (postburial) oxidation of primary reduced iron phases (Rasmussen et al., 2016); however, hydrogeological modelling suggests that largescale, basin-wide secondary oxidation of iron in this type of setting is unlikely (Robbins et al., 2019).

Three popular models have been proposed to account for the inferred early submarine oxidation of ferrous to ferric iron, and the resulting deposition of BIF: (1) photochemical oxidation via ultraviolet radiation (Cairns-Smith, 1978), (2) oxidation with free oxygen, and (3) microbial iron oxidation (Widdel et al., 1993). Photochemical iron oxidation is a viable mechanism but is outcompeted by chemical reactions of iron with silica, or bicarbonate, which form the ferrous iron minerals greenalite [Fe₃Si₂O₅(OH)₂] or siderite (FeCO₃), respectively (Konhauser et al., 2007). Oxidation of iron with free oxygen is difficult to reconcile with an effective absence of free oxygen in the atmosphere in the Archean, prior to the Great Oxidation Event (GOE) ca. 2400-2300 Ma (evidence reviewed in (Lyons et al., 2014)), although oxygen oases may have endured in some shallow marine environments during the Archean (Olson et al., 2013). Finally, the rarity of fossils and minimal levels of organic matter present in BIF (Dodd et al., 2019; Klein, 2005) have led some workers to question the role of microbes in iron oxidation and deposition, although small organic matter contents of microbial iron stalks (Chan et al., 2011) or the diagenetic oxidation of organic matter as indicated by Fe and C isotopes of iron minerals, could also explain the low concentrations of organic matter in BIF (Heimann et al., 2010; Johnson et al., 2008; Konhauser et al., 2017). In contrast, studies of modern and Phanerozoic hydrothermal iron deposits show ample evidence for microbial activity in the form of fossilized iron-oxide microbial stalks or sheaths (Chan et al., 2011). Other models for the oxidation of ferrous iron in the early oceans involve the oxidation of iron by H₂O₂ produced either through radioactive decay of primordial ⁴⁰K, ^{235/238}U, and ²³²Th (Ershov, 2021) or by photolysis of water in the atmosphere (Pecoits et al., 2015). The oxidation of ferrous iron by H₂O₂ as a result of photolysis has been questioned based on atmospheric chemistry models, which show that H₂O₂ fluxes were likely too low to account for the depositional rates of ferric iron in BIF (Pecoits et al., 2015). Moreover, if radioactive decay within the oceans was generating sufficiently high quantities of H₂O₂ to produce all of the ferric iron preserved in BIF, then H₂O₂ should have also oxidized other reduced species such as dissolved Mn^{2+} or sulfide, producing manganese deposits or elevating ocean sulfate levels, yet manganese deposits are rare in the Archean (Kirschvink et al., 2000) and sulfate concentrations are believed to have been exceptionally low (Crowe et al., 2014). Given the problems with each of the aforementioned models, the potential oxidation of iron in the early anoxic oceans and subsequent deposition of BIF remains a fundamental enigma for many BIF deposits. In this study, we propose a new mechanism involving the abiotic, anoxic oxidation of iron following the decomposition of Fe(OH)₂, which we show here to occur in Archean seawater analogs. This mechanism may have been especially relevant for oxide-facies Algoma-type BIF that likely formed in semi-restricted basins. Our finding and new mechanism also have important implications for iron cycling and oxidation of the early Earth.

2. Background: anoxic oxidation of iron in ferrous hydroxide

Anoxic oxidation of iron (Equ. (1) vs Equ. (2) for oxic iron oxidation) is known to produce magnetite during high-temperature serpentinization reactions (Klein et al., 2013). Prior work has shown that this reaction can also proceed at low temperatures below 100 °C in deionized water or in Fe²⁺-, Mg^{2+} -, and SiO_{2(aq)}-bearing waters (Tosca et al., 2018). Reaction progress is highly variable and slower at temperatures below 100 °C. The presence of certain metals or inorganic and organic compounds, including nickel, copper, cobalt, platinum, sodium sulfide, magnesium hydroxide, sugars, and polyhydric alcohols, may aid the reaction progress, whereas elements such as silicon may hinder its progress (Schrauzer and Guth, 1976; Shipko and Douglas, 1956). Following the nucleation of ferrous hydroxide, Equ. (1) is believed to be favored in neutral to alkaline solutions, between pH 7 and 11, inducing disproportionation of $Fe(OH)_2$ and the formation of elemental iron that may react with water molecules to form H₂ gas and ferric iron (Schrauzer and Guth, 1976). Consequently, the reaction is commonly tracked by measuring hydrogen evolution (Equ. (1)) (Schrauzer and Guth, 1976; Shipko and Douglas, 1956).

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + 2OH^- + H_2$$
Anoxic iron oxidation
(1)
$$2Fe^{2+} + 0.5O + H_2O + 2Fe^{3+} + 2OH^-$$

$$2Fe^{2+} + 0.5O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH$$

(2)

Oxic iron oxidation

In the following sections we explore the decomposition and subsequent oxidation of ferrous hydroxide $[Fe(OH)_2]$ as a potential mechanism for iron oxidation in the Archean anoxic oceans. This work is based on previous experimental observations of ferric iron and hydrogen generation from ferrous hydroxide suspensions in alkaline media (Schrauzer and Guth, 1976; Shipko and Douglas, 1956).

3. Experiments and materials

To test whether the anoxic oxidation of iron could occur in early anoxic oceans, Archean seawater analogs were prepared using appropriate salts dissolved in deionized and deoxygenated water that together mimic the predicted chemistry of the Archean Ocean (Table 1). It has been proposed that the Archean ocean could have had an acidic pH below 7 (Halevy and Bachan, 2017), although some workers have argued for more alkaline conditions (Sleep and Zahnle, 2001). In order for greenalite—a widely accepted primary mineral in BIF (Klein, 2005; Rasmussen et al., 2017)—to precipitate, ocean pH would have needed to be above 7 and likely over 7.25, based on the experimentally determined solubility of greenalite

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Table 1

Composition and typical concentrations of salts used to reconstruct Archean seawater in this study and previous studies. M.S – modern seawater. DIC – dissolved inorganic carbon.

Salt	This study	Chemistry of other experiments simulating BIF genesis		
	(mM)	Halevy et al. (2017) (mM)	Tosca et al. (2016) (mM)	Konhauser et al. (2007) (mM)
Sodium chloride (NaCl)	393.8	420.3	393.8 (M.S)	560
Sodium sulfate (Na ₂ SO ₄)*	2-170	0.1	2	-
Potassium chloride (KCl)	9.1	-	9.1 (M.S)	-
Sodium bicarbonate (NaHCO ₃)	0-40	24.2-48.3 DIC	2.3 (M.S)	2.4-233 DIC
Potassium bromide (KBr)	0.1	-	0.1 (M.S)	-
Magnesium chloride (MgCl ₂ .6H ₂ O)	53.3	49.9	53.3 (M.S)	-
Calcium chloride (CaCl ₂ .2H ₂ O)	10.3	-	10.3 (M.S)	0.08-4.59 Ca
Sodium metasilicate (Na ₂ SiO ₃ .9H ₂ O) Ferrous ammonium sulfate	1-2	0.1-0.25	1.25 Si	2.1 Si
(Mohr's Salt) ((NH ₄) ₂ Fe(SO ₄) ₂ .6H ₂ O)	1-85	0.3	1 Fe	1.8 Fe

*Added as Mohr's salt in this study.

Table 2

Information on all experimental runs in this study. Experiments were run in triplicate. Those experiments including DIC were measured only by Gas Chromatography-Mass Spectrometry using gas-tight sealed brown glass bottles.

Experiment	pН	Solution chemistry	H ₂ detected?
1	8.5	Fe 1 mM; 0 mM DIC; Si 1 mM	Yes
2	8	Fe 2 mM; 0 mM DIC; Si 1 mM	Yes
3	8	Fe 1 mM; 0 mM DIC; Si 1 mM	No
4	7.5	Fe 1 mM; 0 mM DIC; Si 1 mM	No
5	7.5	Fe 25 mM; 0 mM DIC; Si 1 mM	Yes
6	7.25	Fe 85 mM; 0 mM DIC; Si 1 mM	Yes
7	8.5	Fe 2 mM; 5 mM DIC; Si 1 mM	Yes
8	8.5	Fe 2 mM; 10 mM DIC; Si 1 mM	Yes
9	8.5	Fe 2 mM; 20 mM DIC; Si 1 mM	No
10	8.5	Fe 2 mM; 40 mM DIC; Si 1 mM	No
11	8.5	Fe 2 mM; 0 mM DIC; Si 2 mM	Yes
12	8.5	Fe 1 mM; 0 mM DIC; Si 2 mM	Yes
13	8.5	Fe 1 mM; 0 mM DIC; Si 0.4 mM	Yes
14	8	Fe 2 mM; 0 mM DIC; Si 0.4 mM	Yes
15	7.5	Fe 25 mM; 0 mM DIC; Si 2 mM	Yes
16	7.25	Fe 25 mM; 0 mM DIC; Si 1 mM	No

Table 3

Quantitative H_2 detection by Gas Chromatography-Mass Spectrometry. Experiments were conducted at a starting pH 8.5; see Methods for further details. All experiments were conducted in triplicate with range of H_2 values shown. DIC – dissolved inorganic carbon.

Fe^{2+} , SiO ₂ (aq), DIC concentration in seawater	H_2 produced (µmol H ₂ /mmol Fe) \pm 5%
2 mM Fe + 1 mM Si	190-215.2
2 mM Fe + 2 mM Si	22.3-25.6
2 mM Fe + 1 mM Si + 5 mM DIC	3.6-4.1
2 mM Fe + 1 mM Si + 20 mM DIC	None detected
2 mM Fe + 1 mM Si + 40 mM DIC	None detected

(Tosca et al., 2016). Given that the reaction of Equ. (1) is only viable above pH 7 (Schrauzer and Guth, 1976; Shipko and Douglas, 1956), a pH range of 7.25 to 8.5 was chosen for the experimental runs (Table 2). Hydrogen evolution from the reaction solutions was measured semi-quantitatively by an electrochemical hydrogen gas sensor, and quantitatively by gas chromatography-mass spectrometry (Table 3), in order to determine the reaction progress, in addition to periodic sampling of the solution for chemical analysis (Fig. 1).

3.1. Anoxic iron oxidation experiments

A three-necked flask with sintered gas bubbler was set up in a sealed system of tubing, with silicone oil traps used at either end to prevent air flow into the system (Fig. 1). A connector fit-

ted to the top of the reaction flask was split into three separate outlets, two fitted with Suba-Seals® and the third with a solid tube used for addition of reagents. The flask was wrapped in aluminium foil to prevent UV-photooxidation of reagents. A pH meter and syringe containing deoxygenated 1M NaOH solution was inserted into the top of the connector. Each joint in the flask necks was wrapped in polytetrafluoroethylene tape to ensure an airtight fit. The flask was filled with 1 L of deionized water, and various salts were added (Table 1) to simulate early ocean chemistry. After addition of the salts, $(NH_4)_2 Fe(SO_4)_2 \cdot 6H_2O$ was then weighed and loaded into a solid addition tube, and the system was sealed. Argon gas of 99.999% purity was then passed through the system for at least 1 hr with vigorous stirring of the solution to remove dissolved oxygen. Due to the continuous purging of the solution with Ar gas, the experiments using varying concentrations of dissolved inorganic carbon were conducted with sealed containers in an anoxic chamber (see below). Extracts of the solution were taken by syringe and analyzed for dissolved oxygen with the Winkler test, which gave values of 0.3-0.6 mg/L dissolved O₂. After at least 1 hr of bubbling, a Chang-AI Intelligent Analyzer hydrogen sensor was connected to the gas outflow tube and the Ar gas flow was then stopped. The $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was then added to the solution by inverting the solid addition tube, the solution being continuously stirred using a magnetic stir bar. To start the experiment, 1M NaOH was added dropwise to the solution to raise the pH to the desired level. The precipitation of ferrous hydroxide consumed hydroxyl and led to a lowering of pH, therefore 1M NaOH was added manually to maintain a constant pH. After 1 hr of continuous stirring, the Ar gas was passed through the solution again and the H₂ concentration of the output gas was measured using the Chang-AI Intelligent Analyzer hydrogen sensor. A second measurement was made after 2 hrs. Throughout the duration of the experiment, 1 ml aliquots of sample were periodically taken and diluted with 2% HNO3 for analysis by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) for Na, K, Mg, Ca, Si, and Fe. Concentrations of all elements had reproducibility better than 6% based on repeated measurements of internal standard solutions. In order to verify the oxidation state of the dissolved Fe, a portion of the same extracted aliquot was measured for Fe^{2+} using the 1,10-phenanthroline spectrophotometry method, which had reproducibility better than 5% based on repeated measurements of internal standard solutions; the concentration of Fe²⁺ was within error of the Fe concentration determined by ICP-OES.

The Chang-Al Intelligent Analyzer hydrogen sensor (detection limit 1 ppm H_2) was used to semi-quantitatively measure hydrogen production, and thus the progress of equation (1). This sensor was calibrated using pre-mixed H_2 and Ar gas mixtures, with H_2 concentrations ranging from 1 to 10 ppm. The error on H_2 con-



Fig. 1. Schematic of experimental apparatus and setup used in this study. Argon gas passes through a silicone oil trap and enters the solution via a glass bubbler. The gas subsequently exits through another silicone oil trap and enters a H₂ sensor. The silicone oil traps prevent air entering the reaction vessel.

centration readings was ± 0.5 ppm. Argon gas bubbled through the reaction flask was measured using the same hydrogen sensor and confirmed to be below the detection limit of H₂ (<1 ppm).

3.2. Quantitative H₂ determination by Gas Chromatography-Mass Spectrometry (GC-MS)

In order to quantify the amount of H₂ produced during the decomposition of ferrous hydroxide in synthetic seawater, and to assess the effects of dissolved inorganic carbon on the decomposition reaction, sealed flasks of seawater were prepared in an anoxic glove box. In preparing the experimental solutions, appropriate salts (excluding iron and bicarbonate salts; Table 1) were dissolved in deionized water. The solution was then purged of dissolved oxygen by bubbling 99.999% N_2 gas through it for 2 hrs. The solution was then transferred into an anoxic glove box that had previously been purged with N₂ gas to remove O₂ and H₂ gases. The solution was then purged with N₂ gas for a further 1 hr inside the glove box. The solution was then divided into 0.5 L flasks and $(NH_4)_2$ Fe $(SO_4)_2 \cdot 6H_2O$ was added, while maintaining a pH just below 7. Then NaHCO₃ was added to the solution and the pH was immediately adjusted to the desired value using a deoxygenated 1M NaOH solution. The resultant solution was then immediately divided into aliquots of 0.5 L and transferred into 0.5 L brown bottles with septum caps, making sure to leave no headspace for CO₂ to degas into. Two bottles were left empty inside the anoxic glove box to capture only gas from inside the chamber. The gas inside the bottles was then measured for H₂ to establish background H₂ gas concentrations, which were in both instances below detection. After 24 hrs, a syringe was used to extract 5 ml of solution through the septum cap and the bottles were then shaken to displace dissolved gas to the headspace. The headspace gas was then extracted through the septum cap by a gas-tight syringe and injected into an Aligent GC-MS system to measure the amount of H_2 gas, at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Owing to the gradual precipitation of ferrous hydroxide, the solution pH decreased with time and after 24 hrs the pH had dropped from 8.5 to 8.1. This pH decrease could not be stopped after the solutions were sealed in the bottles. Therefore, the reported H₂ yields are likely lower than what would be expected because lower pH increases the solubility of ferrous hydroxide, hence the reported H₂ yields should be regarded as minimum values.

3.3. X-ray diffraction of experimental precipitates

Following the same procedures as outlined above for quantitative H_2 determination, synthetic seawater solutions were divided into 1 L flasks and $(NH_4)_2$ Fe(SO₄)₂·6H₂O was added inside an anoxic glove box, while maintaining a pH just below 7. The solution was continuously stirred using a magnetic stir bar. To start the experiment, 1M NaOH was added dropwise to the solution to raise the pH to the desired level. During the experiment, the precipitation of ferrous hydroxide consumed hydroxyl and led to a lowering of pH, therefore 1M NaOH was added manually in order to maintain a constant pH of 8.5. After 2 hrs, the solution was filtered, and the precipitate washed in deoxygenated ultra-pure water inside the anoxic glove box.

The precipitate was then mounted on glass slides and sealed in Kapton foil within the anoxic glove box to prevent oxidation of the precipitate during analysis by X-ray diffraction (XRD) in air, using a Dandong Tongda TD3500 X-ray diffractometer at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan. XRD data were collected at 45 keV and 35 mA from 3 to 65° 2θ in steps of 0.02°. The resultant diffraction pattern was corrected, and phases present identified, by comparing the observed diffraction peaks with those of possible run products. Subsequently, the data were processed using the JADE software package that validated this mineralogical interpretation.

4. Results and discussion

4.1. Anoxic iron oxidation in the Archean anoxic seawater analogs

Hydrogen gas was detected in all reactions when conditions led to saturation and precipitation of ferrous hydroxide, except when DIC concentrations exceeded 20 mM (Table 1 and Table 2). When ferrous hydroxide saturation was reached, Fe^{2+} concentrations dropped rapidly (over 10 s of minutes) until reaching equilibrium at values consistent with the solubility of ferrous hydroxide (Fig. 2A). The concentration of dissolved Si also declined in tandem with Fe^{2+} concentrations, which might imply that iron-silicate phases were precipitating. Under the experimental conditions used, iron silicates are expected to precipitate over hundreds of hours (Tosca et al., 2016), whereas in this study Si and Fe concentrations



Fig. 2. Solution chemistry for anoxic iron oxidation in this study. (A) Concentration of dissolved elements in the experimental solution over the course of the reaction at pH 8.5; and (B) at pH 7.5. Note, all elemental concentrations remain consistent with initial concentrations throughout duration of the experiment except for Fe and Si at pH 8.5. At pH 7.5, Fe and Si also remain at constant concentrations.



Fig. 3. X-ray diffraction (XRD) pattern of washed and dried precipitate collected from the reaction vessel two hrs after starting the experiment. XRD pattern is consistent with green rust (GR).

dropped rapidly, reaching equilibrium in under 1 hr. However, Si and Fe concentrations were found only to decline over an hour when ferrous hydroxide solubility was breached (Fig. 2A-B). No iron silicates were detected by XRD in the precipitates formed (Fig. 3) but may have been too disordered to be identified. Therefore, the observed drop in Si concentrations could be due to Si adsorption onto ferrous hydroxide precipitates or Fe-silicate precipitates, or onto a combination of both.

XRD analysis of the precipitates indicates a predominance of green rust (Fig. 3), which is the expected product following the decomposition of ferrous hydroxide. Green rust has been reported as an experimental run product in other studies as a result of ferrous hydroxide decomposition (Schrauzer and Guth, 1976; Shipko and Douglas, 1956; Tosca et al., 2018), or reaction of ferrous iron with restricted quantities of free O_2 or ferric iron (Halevy et al., 2017; Li et al., 2017). The precipitate mineralogy documented in this report, together with the detection of hydrogen gas, provides compelling evidence for the breakdown of ferrous hydroxide into

mixed-valence, iron-oxide phases in the Archean anoxic seawater analogs.

In the experiments, both semi-quantitative and quantitative determination of hydrogen gas concentrations show that increasing contents of dissolved Si or dissolved inorganic carbon (DIC) decreased hydrogen gas yields (Table 2 and 3). Quantitative analysis of hydrogen gas in sealed containers was used to explore the effects of DIC on hydrogen yields and to more accurately estimate the effects of solution chemistry on the progress of Equ. (1). A doubling of Si concentrations from 1 to 2 mM led to a 10-fold reduction in hydrogen gas yields; the addition of 5 mM DIC produced an almost 60x reduction in hydrogen gas yields. No hydrogen gas was detected in the experimental runs using 20 and 40 mM DIC (Table 1), whereas semi-quantitative measurements indicate that hydrogen gas was still being produced at concentrations of 10 mM DIC (Table 2). Based on the quantities of H_2 gas detected (Table 1) and the molar stoichiometry of H_2 and Fe^{3+} production in Equ. (1), the minimum quantities (see Methods) of ferric iron produced per mole of ferrous iron ranged from 3.6 to 215.2 μ M.



Fig. 4. Solubility diagram showing relative solubility of ferrous hydroxide (after Feitknecht and Schindler, 1963) and greenalite (after Tosca et al., 2016).

In summary, if ferrous hydroxide saturation is reached, this phase can precipitate and undergo a disproportionation reaction to form elemental iron and subsequently ferric iron and hydrogen gas under plausible Archean seawater chemistries. However, the reaction yield is highly variable depending on solution chemistry (Table 1), with both DIC and silica (Table 1) repressing the hydrogen yield. The variable production of hydrogen gas due to the presence of silica is postulated to result from the formation of ferrous silicates on the surface of ferrous hydroxide (Shipko and Douglas, 1956). It has also been speculated that Fe(OH)₂ precipitates have variable crystallinities that result in a range of reactivities (Schrauzer and Guth, 1976). This crystallinity control on reactivity has been inferred on the basis of the experimental addition of complexing or dispersing agents during the precipitation of Fe(OH)₂, leading to variable H₂ yields. This outcome was attributed to the stabilization of disordered aggregates of Fe(OH)₂ that may be more reactive than ordered aggregates of Fe(OH)₂ (Schrauzer and Guth, 1976). It is therefore possible that higher concentrations of silica and DIC interfere with the Fe(OH)₂ chemical structure, and hence its aging process and decomposition to elemental iron and H₂ yields. Alternatively, the precipitation of Fesilicates or carbonates could have removed available Fe for ferrous hydroxide precipitation thereby diminishing H₂ yields.

4.2. Implications for Archean BIF formation

4.2.1. Conditions for anoxic iron oxidation in Archean ocean basins

The potential spontaneous oxidation of ferrous hydroxide to ferric iron has important implications for planetary iron cycling on early Earth and the genesis of Archean BIF. A critical resulting question is: did early ocean chemistry satisfy ferrous hydroxide saturation? The solubility of ferrous hydroxide is primarily a function of solution pH and Fe^{2+} concentration (Fig. 4). Under a range of pH values typical of the modern ocean (8.5-7.5), Fe²⁺ concentrations of about 0.2 to 20 mM, respectively, are required in order to reach ferrous hydroxide saturation. Based on δ^{56} Fe data from BIF in the Transvaal of South Africa, isotopic mass-balance models suggest that Archean seawater Fe²⁺ concentrations may have reached 37 mM during periods of BIF deposition (Thibon et al., 2019), thus easily accommodating ferrous hydroxide saturation down to pH values of 7.4. Based on our experimental results, Fe(OH)2 will precipitate and decompose, forming H₂ gas at alkaline pH values as low as 7.25 and possibly lower (Tables 2-3) (Schrauzer and Guth, 1976). Because primary minerals in BIF require neutral to mildly alkaline seawater in order to precipitate (Grotzinger and Kasting, 1993; Jiang and Tosca, 2019; Tosca et al., 2016), it can be inferred

that the coeval ocean pH was conducive to $Fe(OH)_2$ saturation and decomposition to ferric iron, therefore ocean Fe^{2+} concentration was the key control on saturation state.

Previously it has been proposed that Precambrian seawater Fe^{2+} concentrations under steady-state conditions were buffered by the solubility of siderite, corresponding to values of 0.01-0.12 mM (Grotzinger and Kasting, 1993). This assumption has, however, been recently challenged based on the solubility of ferrous carbonates in ferrous silicate-carbonate systems, suggesting that greenalite, not siderite, was the predominant control on dissolved Fe^{2+} concentrations (Jiang and Tosca, 2019). Consequently, greenalite solubility would likely have buffered ocean Fe^{2+} concentrations to 0.004 and 1.3 mM for pH values of 8.5 and 7.25, respectively.

Whereas greenalite may have been a solubility limiting phase for Fe²⁺ under steady-state conditions, its ability to limit Fe²⁺ concentrations applies only when Fe²⁺ fluxes to the ocean do not exceed Si fluxes by more than 1.5x. This is because greenalite [Fe₃Si₂O₅(OH)₂] consumes 1.5 moles of Fe per mole of Si; therefore if Si becomes limiting, seawater Fe²⁺ would be expected to rapidly increase. A hotter mantle on early Earth would have generated a larger proportion of ultramafic rocks, which in the modern ocean are known to produce hydrothermal fluids with high Fe/Si molar ratios above 3 (Douville et al., 2002). This result would have been reinforced by low sulfate concentrations in the Archean ocean that minimized iron sulfide formation and hence could have allowed Fe²⁺ concentrations in hydrothermal fluids to reach 80 mM (Kump and Seyfried, 2005). Consequently, prolonged venting of hydrothermal fluids containing Fe/Si molar ratios over 1.5 would lead, especially in hydrothermally active basins, to the lowering of Si concentrations and suppression of greenalite precipitation, thus greatly enhancing dissolved Fe²⁺ concentrations.

Elevated Eu anomalies (Bekker et al., 2010; Konhauser et al., 2017), depleted Si isotopic signatures (Bekker et al., 2010; Delvigne et al., 2012; Heck et al., 2011; Steinhoefel et al., 2009), and nearzero δ^{56} Fe values in BIF (Bekker et al., 2010; Johnson et al., 2008) have all been taken as evidence for strong hydrothermal controls on the seawater chemistry of ocean basins in which BIF precipitated. Collectively, these observations support the inference that ocean-basin Si budgets where BIF formed were likely controlled by hydrothermal fluxes, in contrast to continental weathering fluxes (Delvigne et al., 2012; Heck et al., 2011). Moreover, microscale and interlayer variation of negative δ^{30} Si values in BIF suggest oscillating local seawater Si concentrations in connection with iron-oxyhydroxide deposition (Delvigne et al., 2012; Heck et al., 2011; Steinhoefel et al., 2009), thus supporting the premise that silica



Fig. 5. Petrographic observations of typical Algoma-type BIF (A-D) and conceptual geological model for banded iron formation (BIF) genesis by anoxic iron oxidation (E). (A) Photomicrograph of micron-sized magnetite delineating spheroids in greenschist-facies, Algoma-type Abitibi BIF (~2.7 Ga; Canada) (Mueller and Mortensen, 2002). Inset is lower-magnification view of panel A (white box). (B) Polished thin section of greenschist-facies, Algoma-type Sandur BIF (~2.7 Ga; India) (Manikyamba et al., 1993) showing magnetite and quartz layers. The layers I, II, and III (red rectangles) correspond to the intervals I, II, and III in (E). (C) Photomicrograph showing mignetite-quartz layers in Sandur BIF. (D) Photomicrograph showing micron- to nanometer-sized magnetite, pyrite, and siderite in Sandur BIF. (E) Illustrative model of BIF formation by anoxic iron oxidation: Interval I: Initially, seawater Fe²⁺ concentrations are buffered to values close to the solubility limit of greenalite (insert of blue line along dashed greenalite solubility line). Silica saturation promotes opal precipitation and the formation of quartz layers. Interval II: A period of hydrothermal activity forces seawater dissolved Fe²⁺ concentrations to saturation with respect to Fe(OH)₂, leading to that the precipitation of Fe(OH)₂ converts to green rust and then possibly ferrous-ferric oxide/silicate/carbonate layers. Interval III: Cessation in hydrothermal activity leads to dissolved Fe²⁺ concentrations dropping below Fe(OH)₂ saturation, and greenalite continues to precipitate until reaching its solubility limit. Mineral abbreviations: Mag – magnetite; Qtz – quartz; Stp – Stilpnomelane; Py – Pyrite. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

concentrations varied during BIF deposition. Consequently, lowering of Si availability and the excess of Fe²⁺ produced during periods of intense hydrothermal activity could have allowed Fe²⁺ concentrations to reach ferrous hydroxide saturation. Maintenance of high Fe²⁺ fluxes would have been promoted especially in basins within or surrounding volcanic arcs, or back-arcs, where dilution by a large volume of low-Fe seawater was minimized. Such settings are known for many Algoma-type BIF, including for iron formations associated with volcanogenic massive sulfide deposits (Bekker et al., 2010). Consequently, Algoma-BIF, which are commonly found with graywacke or associated with exhalites in greenstone belts (e.g., \sim 2.7 Ga Abitibi BIF in Canada and \sim 2.7 Ga Sandur BIF in India), are the best targets for testing whether ferrous hydroxide played a key role in BIF deposition. Similarly, any BIF deposits that preserve strong signatures of hydrothermal chemistry (e.g., Eu anomalies >2 that are common for Archean BIF; (Konhauser et al., 2017)) would also be viable candidates given that a stronger hydrothermal signature likely indicates locally higher Fe²⁺ concentrations during sediment deposition.

In summary, in our model ferrous hydroxide saturation was plausible during periods of intense volcanism and hydrothermal activity within volcanic basins in which BIF precipitated. Whether ferrous hydroxide saturation was attained over expansive areas of continental shelves where Superior-type BIF formed is less certain. Future work that quantifies Archean seawater Fe^{2+} concentrations will be necessary in order to identify the extent of ferrous hydroxide auto-oxidation in the Archean ocean. Moreover, work that addresses the concentration of DIC in Archean seawater and impacts of ferrous carbonate precipitation in the absence of Si will be useful in determining the extent to which DIC affects hydrogen production from ferrous hydroxide precipitation.

4.2.2. Geological model for Archean BIF formation via anoxic iron oxidation

Banded iron formations typically comprise layers composed of magnetite or hematite, iron silicates, carbonates, and chert (Figs. 5A-D). The formation of these iron-rich mineral layers is generally attributed to episodic hydrothermal input (Bekker et al., 2010), with covariation of Fe and Si isotopes supporting a model of periodic hydrothermal precipitation events (Steinhoefel et al., 2009). Consequently, Fe²⁺ concentrations were likely coeval with oscillations in magmatic activity (Thibon et al., 2019) and with the formation of subseafloor large igneous provinces (Bekker et al., 2010). During a BIF depositional sequence, periods of hydrothermal quiescence and low Fe²⁺ fluxes may have resulted in greenalite buffering ocean Fe²⁺ concentrations, a process that would pro-



Fig. 6. Timeline depicting the temporal shifts in iron oxidation and its effects on planetary redox state. (A) Predominant mode of oceanic iron oxidation correlated with approximated increase in atmospheric oxygen over Earth history, modified after Lyons et al. (2014). (B) Tonnage distribution of iron-rich sediments over Earth history, from Bekker et al. (2010) and references therein. Tonnage and number of deposits refers to Precambrian and Phanerozoic iron formations, respectively. (C) Ocean cross-section depicting the processes operating under anoxic iron oxidation. Ferrous iron is oxidized throughout the water column, removing ferrous iron. Hydrogen is released from the ocean or converted to methane by methanogens; abiotic hydrocarbons may be formed by abiotic reduction of carbon distally to hydrothermal vent sites. (D) Upwelled ferrous iron to ferricus iron by free oxygen, removing oxygen/oxidants from the ocean.

mote the accumulation of Fe-poor siliceous gels and minor quantities of greenalite or iron silicates on the surrounding seafloor (Figs. 5A-D and 5E-I). A resurgence in hydrothermal activity and elevated Fe²⁺ fluxes would have increased the precipitation rate of greenalite or iron silicates. If rising Fe²⁺ fluxes overwhelmed Si fluxes or the greenalite precipitation rate, a runaway increase in local seawater Fe²⁺ concentrations would have led to saturation with respect to ferrous hydroxide, at which point this phase would become the dominant Fe-mineral precipitate (Fig. 5E-II). As indicated in our experiments, after precipitation, ferrous hydroxide would rapidly (minutes to hours) undergo disproportionation reactions to yield elemental iron then hydrogen gas and ferric iron, a process that may continue to form green rust (Tosca et al., 2018). Green rust may then age into key mineral components of BIF such as nanoscopic ferrous and ferric oxides, iron-carbonate, and Fe-silicates (Fig. 5A-D) (Halevy et al., 2017; Tosca et al., 2018). A decrease in hydrothermal activity and in the flux of Fe²⁺, together with continual precipitation of greenalite and Fe-silicates, would drop Fe²⁺ concentrations below ferrous hydroxide saturation thus ending the formation of green rust or ferrous and ferric oxides (Figs. 5A-D and 5E-III).

It is proposed here that hydrothermal activity drove oscillating changes in basin Fe²⁺ and Si concentrations leading to alternating greenalite and ferrous hydroxide saturation states, which explains some key petrographic and mineralogical features of BIF. These include compositionally different layers of iron oxide, Fe-silicates, Fe-carbonates, and chert (Fig. 5A-D), but most importantly, the decomposition of ferrous hydroxide provides a key source of ferric iron to proto-BIF sediments. The deposition of ferric iron within BIF sediments may then have undergone microbial or abiotic-diagenetic reactions with organic matter or methane (even with Fe³⁺ bound in ferrous-ferric iron minerals) to form ferrous carbonates with depleted δ^{13} C and δ^{56} Fe values and ferrous-ferric iron

oxides with depleted δ^{56} Fe values (Heimann et al., 2010; Johnson et al., 2008; Konhauser et al., 2005). During later diagenesis, ferrous-ferric iron minerals may recrystallize and grow to the large grain sizes commonly seen in BIF (Fig. 5A), as a result of high temperatures and pressures, a process demonstrated in experimental simulations of BIF diagenesis (Li et al., 2013). While the decomposition of ferrous hydroxide and related green rust formation is one mechanism to explain the occurrence of ferric iron in Archean BIF, it does not necessarily rule out other sources of iron present in Archean BIF sediments. For instance, observations of the Fe isotopic composition of iron oxides in BIF have been used as evidence for incomplete oxidation of ferrous iron via photoferrotrophy or photochemical oxidation (Johnson et al., 2008; Smith et al., 2017; Widdel et al., 1993). These observations and the wide range of depositional settings of BIF highlight the necessity to recognize the potential involvement of multiple mechanisms in the genesis of BIF, and that it is likely no single process can explain all known BIF occurrences. One example is silicate BIF that predominantly comprise ferrous silicates with minimal iron oxides (Klein, 2005). For this BIF facies, there is clearly little need to invoke a mechanism such as ferrous hydroxide oxidation to drive ferric iron to the sediment pile. Consequently, we stress that ferrous hydroxide decomposition is a process most applicable to oxide-facies Algoma-type BIF and thus may not provide a suitable model for other types of BIF. This is especially true when viewing oceanic iron cycling in reference to evolving oceanic and atmospheric chemistry, the timing and aerial development of continental shelves, global glaciations, a cooling mantle, and the evolution of iron metabolisms. All of these parameters may have affected the depositional nature of BIF throughout the Precambrian (Bekker et al., 2010; Klein, 2005; Konhauser et al., 2017) and therefore the processes involved in their formation on an evolving Earth (Fig. 6A-B). We explore this further below in terms of planetary oxidation state.

4.3. Implications for the oxidation of early Earth

In addition to the genesis of Archean BIF, the precipitation and decomposition of ferrous hydroxide to green rust has important implications for planetary oxidation. The generation of hydrogen from anoxic iron oxidation could have sustained early methanogenic archaea, which, if converted to methane (Fig. 6C), would have produced a strong greenhouse effect derived from organic haze (Catling et al., 2001). A portion of the methane alternatively could have been used in iron reduction (Konhauser et al., 2005). Additionally, methane may have been directly produced during BIF deposition through the biological use of Fe⁰ that is produced as an intermediate product in the decomposition of ferrous hydroxide. Previous studies have shown that under anaerobic conditions, methanogens can reduce CO_2 to CH_4 using Fe^0 as an electron donor, which first reduces water to H₂ that subsequently is used to reduce CO₂ (Daniels et al., 1987). Consequently, methanogens may compete for Fe⁰ formed during the decomposition of ferrous hydroxide and reduce the H₂ yield. However, this latter process would increase the ferric iron yield by increasing the portion of Fe⁰ that is oxidized (Fig. 6C). Subsequent photolysis of this methane would have led to hydrogen escape to space and hence planetary oxidation (Catling et al., 2001), or the hydrogen could have directly escaped to space (Fig. 6C).

The tonnage of Archean Algoma-type BIF is estimated at \sim 30,000 Gt, based on the compilation of Isley (1995) and on data for the large deposits of Anshan type in China (Li et al., 2014). Assuming an approximate grade of 30 to 35 wt.% Fe (Bekker et al., 2012, 2010; Klein, 2005) and an average oxidation state of Fe^{+2.4} (Klein, 2005), this equates to 12 to 14 wt.% ferric iron. If all of this ferric iron formed via anoxic iron oxidation, where 2 moles of ferric iron are formed together with 1 mole of H_2 (Equ. (1)), then from estimates of the total Algoma-type Archean BIF tonnage preserved today, 3.2 x 10¹⁶ - 3.8 x 10¹⁶ moles of H₂ could have been produced from this BIF deposition. This simplistic calculation, however, yields a conservative value because the calculation excludes data for the greater mass of iron in Archean Superior-type BIF (80,000 Gt; Bekker et al., 2010) and accordingly the greater mass of H₂ potentially produced from the deposition of these deposits (8.6 x 10^{16} - 1.0 x 10^{17} moles). In addition, this calculation does not include the masses of iron and inferred H₂ related to mostly small Algoma-type deposits that occur in Archean greenstone belts worldwide. Moreover, this estimate for Algoma-type BIF is also low given that the majority of deposits of this type (as well as Superior-type) have been lost through erosion and crustal recycling. In short, hydrogen production from the model of abiotic anoxic iron oxidation proposed herein could have been an important planetary oxidation process during the Archean, counteracting the removal of oxygen by ferrous iron in the early oceans.

Following the rise of atmospheric oxygen after the GOE, iron could have been oxidized by free O₂ (Fig. 6D), therefore diminishing hydrogen release from anoxic iron oxidation and thus decreasing the relative contribution of this mechanism to planetary oxidation. As a result, iron oxidation during BIF formation would switch from being an oxidant supplier to an oxidant sink (Fig. 6A-B). Consequently, ferrous iron—in appropriate geochemical solutions—can be viewed as a planetary oxidant buffer, acting to enhance oxidation under reducing conditions, or acting to promote reducing conditions under oxidizing conditions.

5. Conclusions

The chemistry of BIF deposits provides strong evidence for local seawater compositions having been hydrothermally buffered, which when taken together with the likelihood that Archean hydrothermal fluids had elevated Fe^{2+} concentrations and elevated

Fe/Si ratios, suggests that ferrous hydroxide saturation was entirely plausible within those hydrothermally active basins during BIF deposition. Experimental results presented herein suggest that once formed, the decomposition of ferrous hydroxide could have oxidized ferrous iron independently from microbial activity, dissolved oxygen, H₂O₂, and UV-photooxidation prior to the GOE, thus avoiding the limitations of these previous models. The episodic precipitation of ferrous hydroxide and its subsequent decomposition to ferrous-ferric green rust can explain the formation of many Archean BIF as a simple function of changing mineral saturation states under fluctuating oceanic Fe²⁺ and Si concentrations. Thus, auto-oxidation of ferrous hydroxide provides a new pathway for the genesis of Archean BIF, especially Algoma-type BIF that likely formed in small, restricted, and hydrothermally active basins. Our finding calls for the revision of models for Earth's early biogeochemical iron cycle, for the mechanism for ferrous Fe oxidation involved in BIF deposition, and for planetary oxidation. Future work that reconstructs Archean seawater Fe²⁺ and Si concentrations across intervals of BIF deposition will be crucial in evaluating the extent to which ferrous hydroxide auto-oxidation controlled the Archean iron cycle and the oxidation of the young Earth.

CRediT authorship contribution statement

Matthew S. Dodd: Conceptualization, Funding acquisition, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. Haiyang Wang: Investigation, Validation, Writing – review & editing. Chao Li: Conceptualization, Funding acquisition, Resources, Supervision, Writing – review & editing. Martyn Towner: Methodology, Writing – review & editing. Andrew R. Thomson: Investigation, Validation, Writing – review & editing. John F. Slack: Resources, Writing – review & editing. Yusheng Wan: Resources, Writing – review & editing. Franco Pirajno: Resources, Writing – review & editing. Giang Wang: Investigation, Validation, Writing – review & editing. Opinre Papineau: Conceptualization, Funding acquisition, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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