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► **To cite this version:**

Changle Wang, Leslie Robbins, Noah Planavsky, Nicolas Beukes, Laureline Patry, et al.. Archean to early Paleoproterozoic iron formations document a transition in iron oxidation mechanisms. *Geochimica et Cosmochimica Acta*, 2023, 343, pp.286-303. <10.1016/j.gca.2022.12.002>. <hal-04309466>

HAL Id: hal-04309466

<https://hal.science/hal-04309466v1>

Submitted on 27 Nov 2023

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Archean to early Paleoproterozoic iron formations document a transition in iron oxidation mechanisms

Changle Wang^{1,2,3,*}, Leslie J. Robbins^{2,4*}, Noah J. Planavsky², Nicolas J. Beukes⁶, Laureline A. Patry⁷, Stefan V. Lalonde⁷, Maxwell A. Lechte⁸, Dan Asael², Christopher T. Reinhard⁹, Lianchang Zhang^{1,3}, Kurt O. Konhauser⁵

¹Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China.

²Department of Earth and Planetary Sciences, Yale University, New Haven, U.S.A.

³University of Chinese Academy of Sciences, Beijing, China.

⁴Department of Geology, University of Regina, Regina, SK, Canada.

⁵Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada.

⁶DST-NRF CIMERA, Department of Geology, University of Johannesburg, South Africa.

⁷European Institute for Marine Studies, CNRS-UMR6538 Laboratoire Géosciences Océan, Technopôle Brest-Iroise, Plouzané, France.

⁸Department of Earth and Planetary Sciences, McGill University, Montréal, Canada.

⁹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, U.S.A.

*Corresponding authors: Changle Wang, Leslie Robbins

Email: wangcl@mail.iggcas.ac.cn; Leslie.Robbins@uregina.ca

Abstract

It is generally accepted that photosynthetic marine planktonic bacteria were responsible for the oxidation of dissolved ferrous iron (Fe(II)) and the subsequent deposition of iron formations (IFs) throughout the Archean and early Paleoproterozoic. However, the relative roles of the different biological Fe oxidation mechanisms in driving IF deposition—such as anoxygenic photosynthesis (photoferrotrophs) and oxygenic photosynthesis (cyanobacteria)—remain poorly resolved. Here, we present coupled bulk-rock Fe isotope and manganese (Mn) versus Fe ratios from Archean to early Paleoproterozoic IFs in order to provide a new perspective on Earth's early redox history and processes leading to IF deposition. Based on this updated IF geochemical record, we bolster the case that the partial oxidation of Fe(II) to Fe(III) was central to IF genesis, arguing against extensive water column Fe(II) silicate formation as the main process driving IF deposition. The geochemistry of IFs deposited prior to the Great Oxidation Event (GOE) shows that partial Fe(II) oxidation was a common feature in either anoxic or low oxygen (O₂) conditions, where metabolic Fe(II) oxidation by photoferrotrophs is likely to have prevailed over ambient Fe(II)

37 oxidation by O₂ produced by cyanobacteria. Assuming that cyanobacteria evolved in the Archean,
38 the presence of partial Fe(II) oxidation suggests that O₂ production was relatively muted during
39 this time. This points to a model for Archean surface redox conditions, whereby oxygen oases were
40 relatively limited in extent, likely due to low primary productivity of cyanobacteria and high Fe
41 fluxes. We further demonstrate a gradual displacement of metabolic Fe(II) oxidation in the
42 Archean by quantitative O₂-driven Fe(II) oxidation during the GOE by ca. 2.31 Ga.

43

44 **Introduction**

45 The atmosphere during the first half of Earth's 4.5-billion-year (Ga) history was essentially devoid of free
46 oxygen (O_2), with atmospheric abundances less than 0.001% of the present atmospheric level (PAL) ^{1, 2}.
47 Geological and geochemical constraints reveal that the first permanent rise in the partial pressure of
48 atmospheric O_2 (pO_2) occurred between ~2.5 and 2.3 Ga, a period that has been termed the Great
49 Oxidation Event (GOE) ^{3, 4, 5, 6, 7, 8}. Despite widespread agreement on these general trends, the tempo and
50 mode of Earth's early oxygenation, and the redox conditions leading up to the GOE, remain poorly
51 understood as few redox proxies are sufficiently precise to track secular variations in ocean-atmosphere
52 O_2 abundance. Although incipient oxygenation of Earth's surface environments before GOE has commonly
53 been proposed ^{9, 10, 11}, there still remains an active debate regarding the exact timing of the first emergence
54 of oxygenic photosynthesis ^{12, 13}, with suggestions that this biological innovation may have coincided with
55 the oxygenation of the atmosphere ^{12, 14}. Although, a recent phylogenomic study on enzymes that either
56 produce or utilize oxygen points to an Archean origin for oxygenic photosynthesis ¹⁵. In much the same
57 manner, various geochemical proxies likely have different sensitivities to changes in pO_2 and may not
58 respond uniformly ^{9, 10}, further blurring the history of atmospheric and oceanic pO_2 as well as the exact
59 timing of the GOE. This obscurity in the onset and timing of Earth's early oxidation has also given rise to
60 recent questions as to what role biological oxidation played, if any, in the deposition of iron formations (IFs).

61

62 Iron formations are particularly useful sedimentary archives for tracking Fe sources and sinks during much
63 of the Archean and early Paleoproterozoic as they formed in a range of depositional settings on the
64 continental shelves of existing cratons ^{16, 17}. Moreover, because IF are chemical sediments, they represent
65 an archive of environmental conditions and seawater composition at the time of their deposition ¹⁷, which
66 in turn, provides insights into the availability of trace-element nutrients to, and the activity of, the ancient
67 biosphere ¹⁸.

68

69 The best-preserved IF successions have a remarkably uniform mineralogy, composed mostly of chert,
70 magnetite, and hematite, with variable amounts of Fe-rich silicate minerals (e.g., greenalite), carbonate
71 minerals (e.g., siderite), and locally sparse sulfides (e.g., pyrite). It is also apparent that none of the minerals

72 in IFs today are primary in origin, and that the original seafloor precipitate mineralogy was not preserved.
73 Instead, the observed minerals reflect multiple post-depositional alteration processes that modified the
74 primary precipitates which are generally believed to have been ferric oxyhydroxides (e.g., ferrihydrite) and
75 amorphous silica ¹⁷ (see *Supplementary Materials* for a detailed discussion on the primary mineralogy of
76 IF).

77
78 The presence of ferric iron (Fe(III)) minerals in IFs is generally ascribed to the metabolic activity of
79 planktonic bacteria in the photic zone of Earth's ancient oceans. The classic model invokes Fe(III)
80 precipitation occurring at the interface between oxygenated shallow waters and reduced upwelling ferrous
81 iron (Fe(II))-rich waters, the oxygen (O₂) being sourced from cyanobacteria, or their predecessors ¹⁹. These
82 photoautotrophs would have flourished when nutrients were available and passively induced the
83 precipitation of Fe(III)-oxyhydroxide through the excretion of their metabolic waste (i.e. O₂). Alternatively,
84 anoxygenic photoautotrophic Fe(II)-oxidizing bacteria (known as photoferrotrophs) could have directly
85 oxidized Fe(II) and coupled this to the fixation of carbon utilizing light energy ²⁰. From a mass balance
86 perspective, either metabolism could account for all the Fe(III) deposited in BIF ^{21, 22}. The classical view,
87 however, has recently been challenged, with the suggestion that IFs were largely deposited as Fe(II)
88 silicates (see ²³), a model which would negate the need for oxygenic or anoxygenic photosynthesis in IF
89 deposition. Inspired by the apparent necessity for biologically driven redox reactions and IF precipitation,
90 and its potential to provide insights into the oxygenation of Earth in the lead-up to the GOE, here we explore
91 the coupled proxies of Fe isotope and manganese (Mn) to Fe ratios in an effort to better understand the
92 link between IF deposition and the rise of oxygenic photosynthesis during the Archean and
93 Paleoproterozoic.

94

95 **Iron Formation Deposition and Marine Oxygen Levels**

96 As Fe in seawater is soluble under anoxic conditions as Fe(II) and is rendered poorly soluble under oxic
97 conditions, precipitating readily as Fe(III) oxyhydroxides, the secular record of Fe oxidation may potentially
98 be leveraged to track surface O₂ levels ^{4, 24}. One potential means by which we can parse the mechanisms
99 underpinning Fe(II) oxidation in the ancient oceans is through measurement of the relative abundances of

100 the different stable isotopes of Fe in the Fe-oxides of IFs²⁴. This approach is appealing since the kinetics
101 of Fe(II) oxidation are well-constrained and the Fe isotope systematics of Fe(II) oxidation by
102 photoferrotrophs and ambient O₂ are relatively well-understood^{25, 26, 27, 28}. Briefly, partial oxidation of
103 dissolved Fe(II) produces Fe(III)-oxyhydroxides that are enriched in ⁵⁶Fe, typically by 1 to 3‰, leaving the
104 residual dissolved Fe(II) ⁵⁶Fe-depleted, although more rapid oxidation effectively lowers this overall
105 fractionation²⁷. This contrasts with the formation of reduced iron phases (e.g., Fe carbonates and silicates):
106 these pathways are typically considered to involve either a negligible fractionation or a small negative
107 fractionation^{26, 27}, leaving residual dissolved Fe(II) slightly ⁵⁶Fe-enriched. Furthermore, when Fe(II)
108 oxidation is complete and quantitative—where there is a sharp redoxcline and a well-oxygenated surface
109 layer—there is no net fractionation during the formation of Fe(III) oxides²⁵. However, the fractionation
110 factors of Fe isotopes for Fe(II) oxidation by free O₂ and anoxygenic photosynthesis effectively overlap²⁹,
111 making it difficult to clearly recognize the mechanism responsible for Fe(II) oxidation at different points in
112 Earth's history based on solely Fe isotopes. To address this shortcoming, a supplementary record that can
113 be directly tied to Fe(II) oxidation is required.

114

115 Similar to Fe, manganese (Mn) is redox-sensitive and soluble under anoxic conditions. The oxidation of
116 Mn(II) and the subsequent formation of Mn(III/IV) oxides (from herein simply referred to as Mn oxides) in
117 the presence of free O₂ generally requires both higher redox potentials than the oxidation of Fe(II) and the
118 catalyzing activity of a Mn(II)-oxidizing bacteria³⁰. Manganese oxides would also be expected to undergo
119 rapid reductive dissolution in anoxic, Fe(II)-rich seawater. As such, Mn enrichments resulting from either
120 Mn oxide precipitation or a Mn-oxide shuttle to the sediment-seawater interface may be linked to the
121 presence of an oxygenated water column^{11, 31}. Although the sedimentary and diagenetic pathways
122 responsible for the incorporation of Mn into IFs has recently been questioned³², secular trends in the
123 relative enrichment of Mn in IFs are typically tied to marine redox conditions. Therefore, as IFs serve as
124 robust archives of both the Fe isotope and Mn/Fe ratios in the deep time, they may be interrogated to
125 constrain the redox state of local seawater during IF deposition. Importantly, a coupled approach such as
126 this can provide new insights into the presence of free O₂ in seawater which, in turn, argues against possible
127 anaerobic pathways capable of oxidizing Mn(II)^{33, 34}. Such insights are strengthened when a correlation

128 between these two parameters exists. That is to say, these coupled records are capable of tracking the
129 timing and the evolution, of O₂-driven Fe(II) and Mn(II) oxidation across Earth's history.

130

131 **Tracking Iron Oxidation with Iron Isotopes**

132 Here, we present a detailed record of bulk-rock Fe isotopes (reported as the ratio of ⁵⁶Fe/⁵⁴Fe, relative to
133 the IRMM-014 reference material standard in parts per thousand; δ⁵⁶Fe) and Mn/Fe ratios from Archean to
134 early Paleoproterozoic IFs in order to explore the redox dynamics of the early Earth. Data derived from
135 ~770 individual samples include both new results (n = 253) and those obtained from a comprehensive
136 literature survey (n = 517). Samples were passed through a series of strict filters to select for IFs that are
137 most likely to retain a seawater signature (see *Supplementary Materials*). Nearly all samples have a
138 negligible detrital component (< 0.5 wt.% Al₂O₃) and there exists no significant correlation between the
139 paleoredox data (δ⁵⁶Fe values and Mn/Fe ratios) and detrital indicators (e.g., Al₂O₃, Table S3), suggesting
140 that secular variations in redox indicators were not driven by detrital input. The predominance of positively
141 fractionated Fe isotope values in IFs is supportive of genetic models, which invoke precipitation of primary
142 Fe(III)-oxyhydroxide minerals ²⁶, as opposed to primary Fe-silicate minerals ^{12, 23}. Indeed, a recent
143 evaluation of triple Fe isotope systematics in Neoproterozoic to Paleoproterozoic IF and pyrite samples,
144 indicates that the Neoproterozoic would have been characterized by a significant oxidized Fe sink prior to the
145 GOE ³⁵. Aside from being consistent with the Fe isotopic record, the requirement of extensive Fe oxidation
146 is supported by a recent model that has challenged whether post-depositional groundwater flow could have
147 oxidized a significant volume of Fe(II) on reasonable time scales ³⁶. Therefore, we suggest that IF Fe isotope
148 systematics are consistent with the interpretation that the marine biosphere, namely Fe-oxidizing bacteria
149 (e.g., photoferrotrophs or cyanobacteria), were involved in the oxidation of Fe(II) and the subsequent
150 deposition of IFs. Importantly, Fe isotope data also suggest that secular changes may present a valuable
151 tool for tracking changes in the relative importance of the mechanisms underlying marine Fe(II) oxidation.

152

153 To facilitate the discussion of our data, we have split the deposition of IFs into five stages based upon
154 secular variations in their δ⁵⁶Fe values and Mn/Fe ratios (Fig. 1). Although these bins did not emerge from
155 a robust statistical treatment of the data, this binning helps illustrate that there are fundamental shifts in the

156 redox evolution of Earth's early seawater and atmosphere. Stage 1 extends from the Eoarchean into the
157 Paleoproterozoic (>3.3 Ga) and is characterized by highly positive $\delta^{56}\text{Fe}$ values (Fig. 1a), likely the product of
158 deposition under oxygen-limited conditions that favored the partial oxidation of a relatively large marine
159 reservoir of aqueous Fe(II). Also characterized by low Mn/Fe ratios (<0.01) (Fig. 1b), Stage 1 IFs reflect
160 deposition in an anoxic ocean-atmosphere system. This is consistent with evidence from the sedimentary
161 sulfur isotope record, namely the mass-independent fractionation of sulfur isotopes (MIF-S), which is the
162 prevailing geochemical index for an anoxic atmosphere^{1, 37}. Accordingly, the oxidation of Fe(II) that
163 facilitated IF genesis during Stage 1 was likely photoferrotrophy²⁴.

164
165 Compared to Stage 1, IFs deposited during Stage 2 (3.3 to 2.8 Ga) are characterized by lower $\delta^{56}\text{Fe}$ values
166 (Fig. 1a), suggesting either a greater degree of anoxygenic photosynthetic Fe(II) oxidation³⁸ or elevated
167 marine O₂ concentrations. In conjunction with higher Mn/Fe ratios in Stage 2 IFs (Fig. 1b), we propose that
168 the transition to Stage 2 coincides with the emergence and/or increased impact of oxygenic photosynthesis,
169 implying that free O₂-driven Fe(II) oxidation has been active since ~3.3 Ga. Stage 2 encompasses the
170 deposition of four successions suggested to preserve evidence of pre-GOE O₂ oases (i.e. oxygenated
171 shallow seawater)—the 3.2 Ga Fig Tree and Moodies groups in the Barberton Greenstone Belt^{39, 40}, the
172 2.95 Ga Sinqeni Formation in the Pongola Supergroup¹¹, and the 2.94 Ga Red Lake Greenstone Belt. The
173 data from Moodies and Sinqeni IFs also feature a significant negative correlation between Mn/Fe ratios and
174 $\delta^{56}\text{Fe}$ values (Fig. S1), supporting the interpretation that free O₂ began to accumulate in shallow-marine
175 settings during this interval, allowing for Mn(II) oxidation. In the presence of such a shallow-water oxic zone,
176 photoferrotrophs would still have thrived, growing at depth near the base of the photic zone⁴¹. This would
177 allow photoferrotrophs a preferential access to upwelling nutrients owing to their adaption to lower light
178 levels, thus limiting proliferation of cyanobacteria in the surface ocean⁴² and confining cyanobacteria to
179 very near-shore environments where there may have been nutrient input from emergent continents. Further,
180 cyanobacteria expansion would have been held in check by the high Fe(II) concentrations in the upwelling
181 currents because of the oxidative stress resulting from reactions between Fe(II) and O₂⁴³. Indeed,
182 marginalization of cyanobacteria to shallow waters is consistent with limited O₂ production in the
183 Mesoproterozoic ocean, as evidenced by nitrogen (N) isotopes from shales in the Pongola Supergroup⁴⁴ and

184 the lack of a correlation between $\delta^{56}\text{Fe}$ values (up to 1.5‰) and Mn/Fe ratios within the Red Lake banded
185 IF (BIF) (Fig. S1), implying that the redoxcline remained likely above the photic zone. Therefore, the
186 contribution of microaerophilic and nitrate-reducing Fe(II)-oxidizers to Fe cycling⁴⁵ during this stage is
187 considered to be minor. Moreover, while a sharp redox boundary between deep and shallow waters was
188 proposed to exist at the depositional site of IFs from the 3.2 Ga Fig Tree Group⁴⁰, subsequent studies have
189 reported the frequent occurrence of highly positive $\delta^{56}\text{Fe}$ values for these IFs^{46,47}, likely supporting either
190 partial Fe(II) oxidation in a reducing oceanic environment^{46,47} or heterogeneity in ocean redox conditions
191²⁷. It is noted that the ~2.95 Ga granular IF (GIF) in the upper Nconga Formation of the Pongola Supergroup
192 possesses positive $\delta^{56}\text{Fe}$ values and low Mn/Fe ratios⁴⁸. These features are in stark contrast with those
193 observed in the O₂ oases described above, implying that anoxic conditions were prevalent, disrupted by
194 the presence of spatially restricted disequilibrium between the surface oxygenated oceans and reducing
195 atmosphere⁴⁹. To this end, the 3.22 Ga Moodies Group also records depleted C and enriched N isotopes
196 that suggest an oxidative biogeochemical cycle in a terrestrial environment³⁹, consistent with O₂ having
197 been present in local environments near shallow marine oases.

198
199 The Fe isotopes and Mn/Fe ratios of IFs deposited during Stage 3 (~2.8-2.5 Ga) are comparable with those
200 of Stage 1 (Fig. 1). Transient and spatially restricted oxygenation events have also been suggested to occur
201 during this interval based on a wide range of geochemical proxies^{10, 50, 51}. It also needs to be noted that
202 sulfur-rich exhalites in the ~2.7 Ga Abitibi greenstone belt possess highly negative Fe isotope and higher
203 Mn contents, suggesting the presence of O₂ in the upper part of the water column⁵². However, the IF data
204 presented here do not record evidence of oxygenation events, likely due to either sampling bias or the
205 relatively deep-water depositional environments (below storm wave base) of these IFs. Nevertheless, these
206 samples are from fifteen separate, geographically widespread successions (see *Supplementary Materials*),
207 and are thus considered to be fairly representative of this time interval. The common occurrence of positive
208 $\delta^{56}\text{Fe}$ values indicates partial Fe(II) oxidation, coupled with lower Mn/Fe ratios, indicating the widespread
209 presence of fully anoxic conditions. These conditions likely existed in the upper water column with
210 photoferrotophs being the dominant force in driving Fe(II) oxidation. There is no clear relationship between
211 $\delta^{56}\text{Fe}$ values and Mn/Fe ratios during this stage (Fig. S1), further confirming the absence of free O₂ in the

212 water column. A lack of discrete oxygen oases during this period—as suggested by our data—is further
213 consistent with an Archean world characterized by low levels of primary productivity^{53, 54}.
214
215 Stage 4, from 2.5 to 2.4 Ga, is represented by the most laterally extensive deposition of IFs in Earth history
216¹⁷, and is immediately preceded by a “whiff” of oxygen at 2.5 Ga^{9, 55}. The most striking feature in this interval
217 is that $\delta^{56}\text{Fe}$ values and Mn/Fe ratios have substantially decreased and increased, respectively, marking
218 the gradual transition of the dominant IF oxidant from photoferrotrophs to free O₂ (Fig. 1). Specifically, for
219 the coeval and correlative Transvaal (South Africa) and Hamersley (Western Australia) basins, continuous
220 IF records and precise geochronological constraints reveal a clear trend for these proxies (Fig. S9 and S12).
221 This trend reflects changing marine redox conditions across large portions of the continental margins
222 worldwide. The $\delta^{56}\text{Fe}$ values in IFs become more negative towards the latter stage of Stage 4, while Mn/Fe
223 ratios become higher. Significantly, negative correlations between Mn/Fe ratios and $\delta^{56}\text{Fe}$ values are
224 observed for all IF samples (Fig. S2). We suggest that this is the product of gradually increasing O₂ levels
225 within seawater, whereby the negative $\delta^{56}\text{Fe}$ values are linked to a progressive distillation during the
226 drawdown of the Fe(II) reservoir^{31, 56}, resulting in a ⁵⁶Fe-depleted seawater reservoir. A microbially driven
227 benthic Fe shuttle⁵⁷—which preferentially releases light Fe isotopes—may have also contributed to this
228 isotopically depleted Fe(II) reservoir^{27, 58} (see *Supplementary Materials* for a detailed discussion). In either
229 case, these Fe isotope data are compatible with a scenario in which near-complete Fe(II) oxidation is
230 occurring at the redox boundary of a stratified water column²⁵. This suggests that by Stage 4, substantial
231 O₂ had started to accumulate in the surface ocean, permitting the development of a stable redoxcline
232 separating deep anoxic and shallow oxygenated seawater. This is consistent with an increasingly important
233 role of free O₂ via oxygenic photosynthesis in oxidizing Fe(II). In addition, there is also a decline in the
234 magnitude of positive europium (Eu) anomalies, a high-temperature hydrothermal indicator of Fe input,
235 during Stage 4 IFs (Fig. S3). When combined with increasing oxidation, waning hydrothermal Fe input
236 could have contributed to falling Fe(II) levels in seawater, which in turn, would have alleviated Fe toxicity
237 issues for cyanobacteria⁴³. Collectively, these events would accelerate the expansion and proliferation of
238 cyanobacteria⁴², finally giving rise to well-oxygenated surface seawater. Greater O₂ availability could also
239 have benefited microaerophilic and nitrate dependent Fe(II)-oxidizers⁴⁵. Further, a progressive and

240 pervasively oxygenated surface seawater layer would also imply some degree of free O₂ accumulation in
241 the atmosphere assuming gas-water exchange equilibrium. Such equilibrium would be fully consistent with
242 geochemical proxy records for oxidative weathering (e.g., chromium abundance, S isotopes) in rocks since
243 ~2.5 Ga^{8, 59, 60}. At this stage MIF-S signals are still preserved in sedimentary sulfides, although there is an
244 intriguing possibility that the MIF-S signal was intermittent during this period^{5, 8, 60}.

245

246 Stage 5 corresponds with the permanent loss of MIF-S signals between 2.4 and 2.3 Ga, which effectively
247 constrains the full expression of the GOE^{5, 7, 61}. This stage is defined by rare IF deposition and low Mn/Fe
248 ratios (Fig. 1b). We suggest that this reflects the transition from Fe-rich to Fe-poor oceans. This could be
249 linked to either the large-scale oxidative drawdown of the marine Fe(II) reservoir as evidenced by the burial
250 of the giant IF deposits of South Africa and Western Australia, and Fe isotope systematics indicative of
251 Rayleigh fractionation of a significantly diminished Fe(II) pool at the end of Stage 4, or waning hydrothermal
252 Fe(II) input, as shown by weakly positive Eu anomalies observed in the Stage 5 IFs (Fig. S3). The studied
253 IFs and ironstones, for the first time, display a narrow and restricted range of $\delta^{56}\text{Fe}$ values, which are
254 indistinguishable from those of bulk silicate Earth ($-0.5 < \delta^{56}\text{Fe} < 0.3 \text{ ‰}$)^{27, 62, 63}. This observation is an
255 expected consequence of essentially quantitative Fe(II) oxidation within a well-oxygenated surface ocean
256 in gas exchange equilibrium with the high-O₂ atmosphere, consistent with other independent estimates for
257 atmospheric $p\text{O}_2$ ⁶⁴.

258

259 **Modeling ocean-atmosphere O₂ abundance**

260 In order to quantitatively estimate the dissolved O₂ concentration of the surface ocean and corresponding
261 atmospheric $p\text{O}_2$, we focused on shallow-marine GIFs and ironstones, which feature Fe ooids. In contrast
262 to deep-marine BIFs, these facies were deposited in water depths close to, or above, storm and fair-weather
263 wave base in near-shore environments^{16, 17}. This is important because unlike deep-marine settings, shallow
264 seawater is unlikely to be deficient in dissolved O₂ relative to the overlying oxygenated atmosphere. These
265 O₂ oases likely included the 3.2 Ga Fig Tree and Moodies groups^{39, 40}, the 2.95 Ga Sinqeni Formation¹¹,
266 and the 2.94 Ga Red Lake Greenstone Belt, and would have been characterized by shallow oxygenated
267 waters set against a backdrop of prevailing anoxic conditions in both the water column and atmosphere.

268 While oases may have been transient in nature, leading to the generation of 'whiffs' of O₂⁹, modelling has
269 also suggested that they may have been more static and laterally extensive, correlated to areas of high
270 nutrient input or upwelling coastal waters⁵³. In either event, these oases would have been characterized
271 by low dissolved O₂ concentrations on the order of 1-10 μmol/kg⁵³, which could have supported the
272 oxidation of Fe(II) and correspondent deposition of IFs.

273

274 The first appearance of GIFs in the geological record is marked by the ~2.95 Ga Nconga Formation, and
275 followed by the ~2.45 Ga Griquatown and ~2.31 Ga Timeball Hill formations, the latter two spanning a
276 critical interval pertinent to the GOE. The Fe isotope composition of these facies show a progression
277 through time from positive δ⁵⁶Fe values, to a mixture of both positive and negative values, to values
278 negligibly fractionated from bulk silicate Earth (Fig. 1a). Therefore, these facies record a marked shift from
279 partial to quantitative Fe(II) oxidation in shallow seawater around ~2.4 Ga. Assuming gas exchange
280 equilibrium and given that nearly all of Fe in the latter two facies were oxidized ultimately by free O₂, partial
281 Fe(II) oxidation in shallow seawater represents robust evidence for low atmospheric pO₂, whereas
282 quantitative Fe(II) oxidation indicates comparatively higher pO₂. We can use a Rayleigh distillation model
283 (see *Supplementary Materials*) to invert these Fe isotope data for an estimate of the extent of Fe(II)
284 oxidation (Fig. 2a). The results show a statistically significant difference between the Griquatown GIF and
285 Timeball Hill ironstone, of which the latter exhibits δ⁵⁶Fe values that we consider as clear evidence for
286 complete Fe(II) oxidation (Fig. 2a). We can then combine these observations with a statistical model of
287 Fe(II) oxidation kinetics taking into account a wide range of possible marine pH values, surface water
288 temperatures, and variable residence times of water masses within the shallow ocean (see *Supplementary*
289 *Materials*). We find that the Fe isotope signatures observed in the Timeball Hill ironstone are extremely
290 difficult to explain unless the dissolved O₂ concentration of their contemporaneous shallow seawater was
291 above 5 μmol/kg, corresponding to atmospheric pO₂ above ~1-2% PAL. Further, partial Fe(II) oxidation
292 responsible for the deposition of the Griquatown GIF most likely requires dissolved O₂ and atmospheric
293 pO₂ below 1 μmol/kg and ~0.1-0.5% PAL, respectively (Fig. 2b). We also invert the Fe isotope data of those
294 BIFs deposited in Archean-early Paleoproterozoic ocean oases for estimating dissolved O₂ concentration

295 of the photic zone (Fig. 2 and S14). We show that dissolved O₂ was below 1 μmol/kg except for the ~2.34
296 Ga photic zone where levels rose above 5 μmol/kg O₂.

297

298 Our results strongly support a dominantly anoxic world before ~2.4 Ga with local oxygen oases containing
299 < 1 μmol/kg O₂, broadly consistent with previous modeling results for a typical O₂ concentration (1-10
300 μmol/kg O₂) within an Archean oasis^{53, 54}. Given that a dissolved O₂ concentration of 1 μmol/kg is equivalent
301 to a roughly 500-fold oversaturation with respect to an atmospheric pO₂ of ~10⁻⁵ PAL (Fig. 2b), it is
302 reasonable to imagine severe ocean-atmosphere disequilibrium with respect to O₂ on a reducing Archean
303 Earth surface within biologically productive regions of the ocean. Assuming that the carbon export flux from
304 the photic zone was dominated by oxygenic photosynthesis in local oases, such a low O₂ state necessitates
305 that net primary productivity be significantly lower than that of equivalent modern environments, especially
306 given the expectation of increased carbon burial efficiency during the Archean⁶⁵.

307

308 As the export flux can also be expected to respond to rates of primary productivity, which are in turn limited
309 by the recharge of nutrients (e.g., phosphorus (P) and N), low dissolved O₂ concentrations require sustained
310 low nutrient conditions prior to ~2.4 Ga. For instance, mass balance considerations have shown that for the
311 Proterozoic, depressed net primary productivity, driven by P limitation, is necessary to maintain a low
312 oxygen state⁶⁵; there is no reason to expect that this should be different prior to the GOE. If P is considered
313 to be the nutrient ultimately controlling marine primary productivity in the Archean and early
314 Paleoproterozoic oceans⁶⁶, there should be a clear difference with respect to the oceanic inventory of P
315 before and after ~2.4 Ga. A subtle distinction in this regard, is the difference between the overall size of the
316 P reservoir through time and how much is available or accessible to the biosphere. While IFs have provided
317 evidence for a sizeable P reservoir⁶⁷, the record of shallow marine environments stands in stark contrast
318 suggesting that P limitation characterized much of Earth's history⁶⁸. This difference may reflect the
319 enhanced sequestration of P by Fe-phases (oxides, green rusts, vivianite)⁶⁸, or the limited recycling of P
320 during biomass remineralization⁶⁹. In either event, this would have limited the P available to primary
321 producers in shallow waters and imposed a direct effect on the degree of primary productivity and, by
322 extension, O₂ production. Based on previous Earth system model simulations⁵³, the predominantly anoxic

323 surface ocean implies that the oceanic P inventory of the Archean may have been as low as 25% of the
324 modern, whereas P levels similar to, or higher than, the modern may have resulted in the establishment of
325 a well-oxygenated surface ocean at ~2.31 Ga.

326

327 **Conclusions**

328 In sum, our findings provide new and complementary insights into how the redox structure of the ocean and
329 atmosphere varied through the Archean to early Paleoproterozoic (Fig. 3). Coupled Fe isotope and Mn/Fe
330 ratio data in IFs extend the first production and local accumulation of O₂ in the ocean to at least the latest
331 Paleoproterozoic, and, when viewed in light of MIF-S signals⁴⁶, further confirm that oxygenic photosynthesis
332 was active well before the first permanent oxygenation of the atmosphere during the GOE and that free O₂
333 produced via oxygenic photosynthesis started to play a role in regulating the oxidation of marine Fe(II) since
334 ~3.3 Ga. However, despite the early presence of cyanobacteria, they probably had no critical direct effect
335 on marine Fe cycling initially, and photoferrotrophy remained the dominant mechanism for Fe(II) oxidation
336 in the Archean ocean, as oxygenated shallow seawater oases in the Archean were transient and spatially
337 restricted.

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339 Importantly, our results argue for a pervasive oxygenation of the shallow ocean during the GOE, with
340 dissolved O₂ concentrations in surface ocean increasing from below 1 to at least 5 μmol/kg. This clearly
341 marks the revolutionary and progressive transition of the dominant oxidative mechanism of marine Fe(II)
342 from photoferrotrophy to free O₂ produced via cyanobacteria at this time. Such a transition could have been
343 closely linked to the growing degree of net primary productivity in the marine environments, ultimately
344 contributing to the progressive, and permanent, oxidation of Earth's surface oceans and atmosphere.

345

346 **Materials and Methods**

347 IF samples were collected from surface outcrop and drill holes and prepared as polished thin sections and
348 analyzed using reflected light microscopy, Raman spectroscopy, and scanning electron microscopy. Well-
349 preserved IF samples were crushed in an agate mill to a fine powder, and sample powders were digested
350 for bulk rock geochemical analyses. Major and trace element compositions were determined using an

351 inductively coupled plasma-mass spectrometer (ICP-MS). For Fe isotope analysis, Fe was purified from
352 sample solutions using ion-exchange chromatography and measured using a multi-collector ICP-MS. Refer
353 to *Supplementary Materials* for detailed methods. All data discussed in the paper are included in
354 Supplementary Tables S1–S2.

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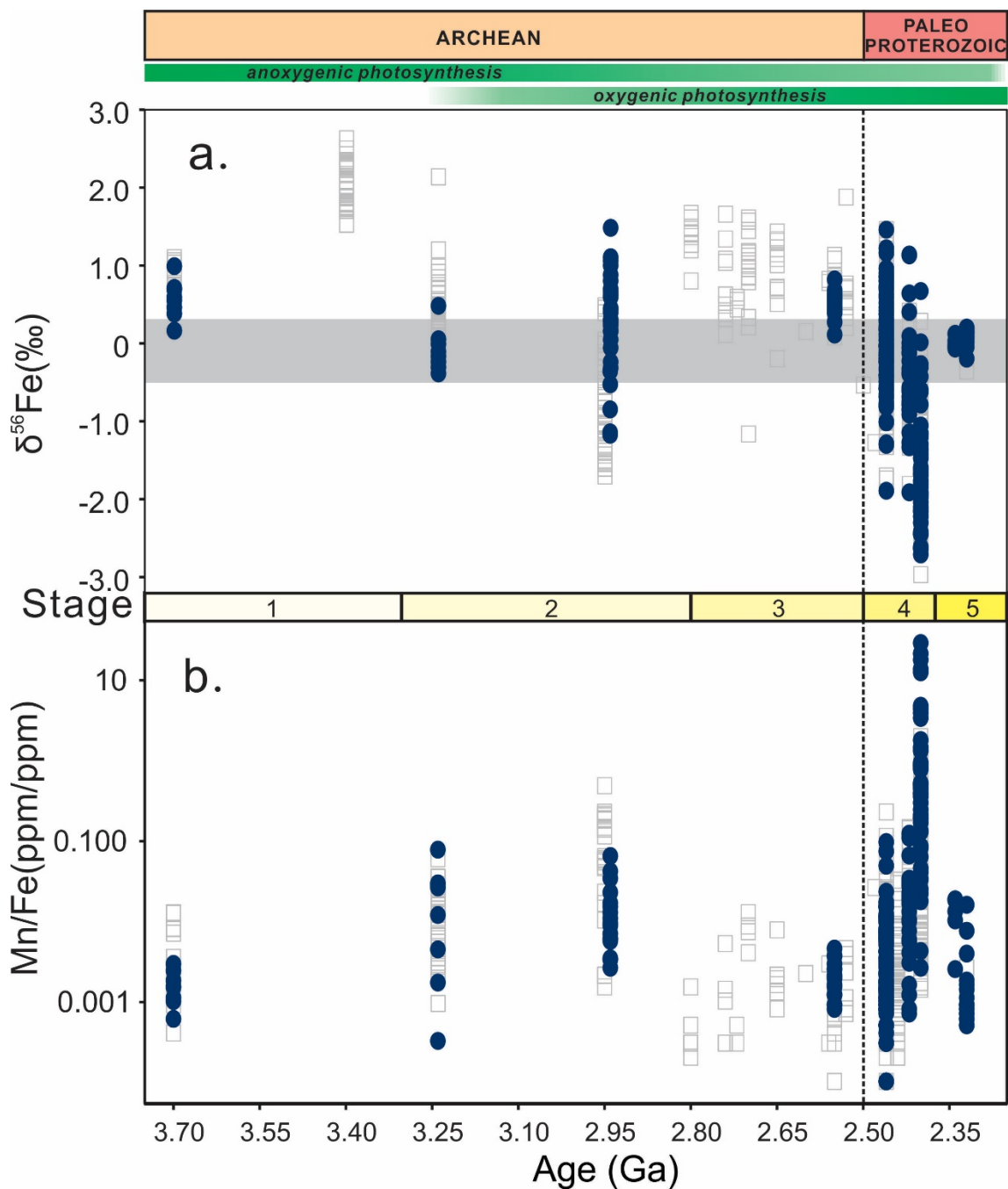
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377 **Figures**

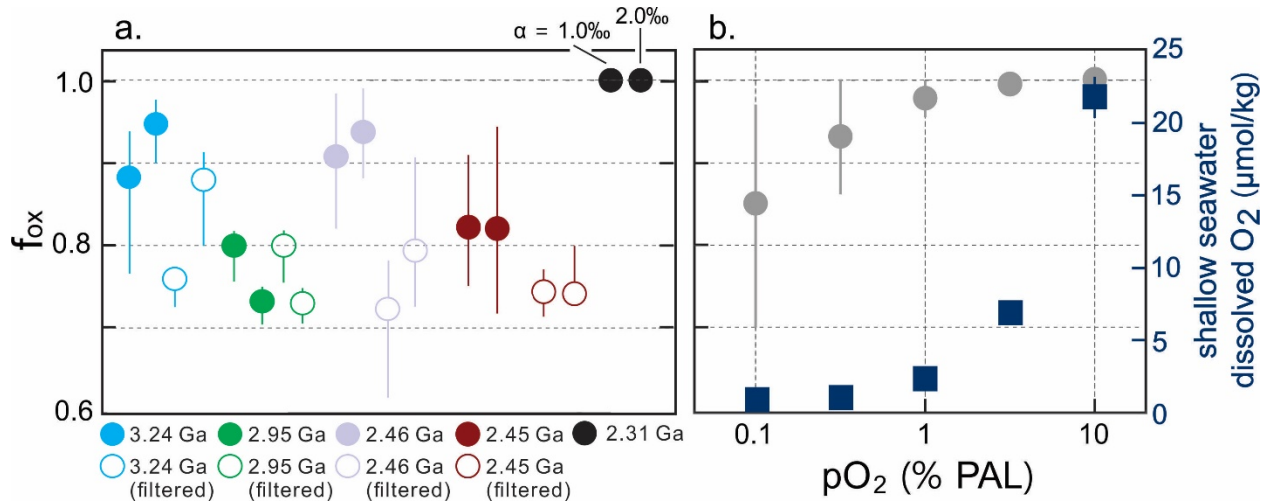


378

379 **Fig. 1.** Temporal variations in $\delta^{56}\text{Fe}$ values (a) and Mn/Fe ratios (b) of bulk Archean and Paleoproterozoic
380 iron formations, ferruginous cherts, and ironstones. Filled blue circles represent new results; unfilled gray
381 squares indicate previous results. Detailed sources of these data are provided in the *Supplemental*

382 *Materials*. Sample standard error is smaller than the data points. Horizontal gray bar denotes the range of
 383 $\delta^{56}\text{Fe}$ values of lithogenic and hydrothermal Fe(II) sources ($-0.5 < \delta^{56}\text{Fe} < 0.3 \text{ ‰}$)^{27, 62, 63}. Note the
 384 logarithmic scale in (b).

385



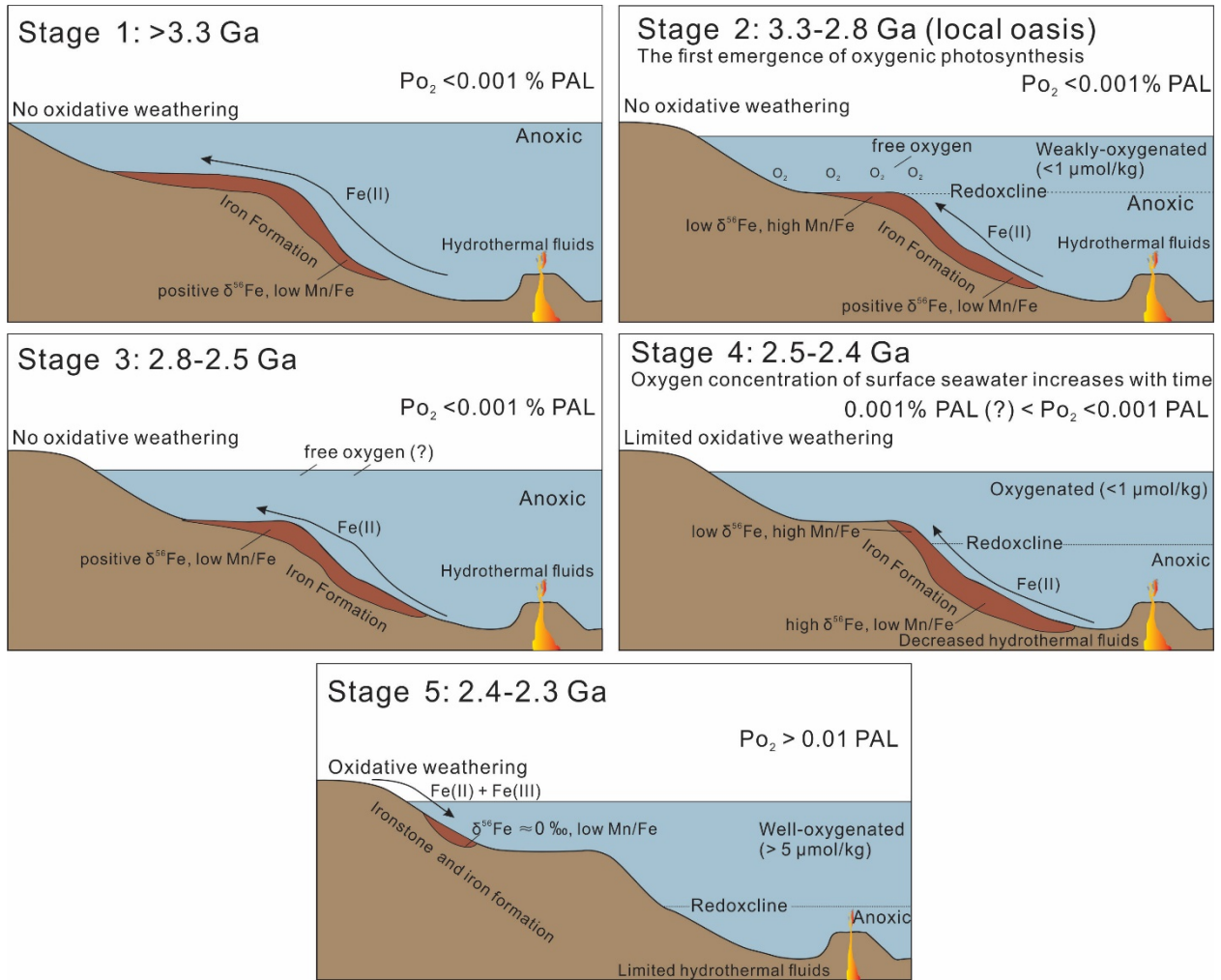
386

387 **Fig. 2.** A model for Fe(II) oxidation in the ~3.24 Ga Moodies BIF, ~2.95 Ga Sinqeni BIF, ~2.46 Ga BIFs in
 388 western Australia and South Africa, ~2.45 Ga Griquatown GIF, and ~2.31 Ga Timeball Hill ironstone as a
 389 function of dissolved O_2 abundance of the surface ocean or photic zone. Shown in (a) are estimates of the
 390 fraction of Fe(II) oxidized in shallow marine environments (f_{ox}) based on a Rayleigh distillation model
 391 assuming two overall isotope effects ($\alpha = 1.0$ (left) and 2.0‰ (right)) for the combined processes of Fe(II)
 392 oxidation and precipitation as Fe(III)-(oxyhydr)oxides (see *Supplementary Materials*). Results are shown
 393 for the combined data (filled circles) and data filtered to exclude non-fractionated samples (open circles).
 394 Error bars show $\pm 1\sigma$ for the entire subsampled dataset. Shown in (b) are results from a kinetic model of
 395 Fe(II) oxidation, resampled 10,000 times at each atmospheric pO_2 value (relative to PAL) across a range
 396 of seawater pH and temperature values. Note that every pO_2 value corresponds to one shallow seawater
 397 dissolved O_2 concentration ($\mu\text{mol/kg}$) assuming gas-water exchange equilibrium. Error bars show $\pm 1\sigma$. Also
 398 note that partial Fe oxidation during the Archean is indicative of low net primary productivity. The
 399 systematics of the observed ~2.45 Ga samples are difficult to explain unless dissolved O_2 and atmospheric
 400 pO_2 were below 1 $\mu\text{mol/kg}$ and ~0.1 % PAL, respectively, while the ~2.31 Ga Timeball Hill data imply
 401 dissolved O_2 at least 5 $\mu\text{mol/kg}$ and a minimum atmospheric pO_2 of ~1% PAL during GOE.

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406 **Fig. 3.** Schematic diagram showing the temporal progression of oxygenation of the Archean to early
 407 Paleoproterozoic ocean and atmosphere.

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416 **ACKNOWLEDGMENTS:** The manuscript benefitted from discussions with Andrey Bekker. We also
417 acknowledge Xuefang Wu for helping to measure Fe isotopes and Andrey Bekker for providing the Timeball
418 Hill samples. **Funding:** This work was supported by grants from the Key Research Program of the Institute
419 of Geology and Geophysics, CAS (grant IGGCAS-201905), National Natural Science Foundation of China
420 (grant 41872087 and 41890833), Youth Innovation Promotion Association, Chinese Academy of Sciences,
421 and China Scholarship Council to C.L.W. S.V.L. and L.A.P. acknowledge support from the European
422 Union's Horizon 2020 research and innovation programme (grant agreement no 716515 to S.V.L.). **Author**
423 **contributions:** C.L.W. and N.J.P. conceived the study. C.L.W. processed the samples. C.L.W. and D.A.
424 conducted geochemical analyses. C.L.W., N.J.B., S.V.L., L.C.Z., and K.O.K. collected samples for this
425 study. L.A.P. provided additional new data for Red Lake samples. N.J.P. and C.T.R. are responsible for the
426 iron oxidation calculations. All authors contributed to writing and editing the manuscript. **Competing**
427 **interests:** The authors declare no competing interests. **Data and materials availability:** All data used in
428 the paper are either tabulated in the Supplementary Materials or published in the cited references.

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