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Triple iron isotope constraints on the role of ocean iron sinks in early atmospheric oxygenation

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Abstract :

The role that iron played in the oxygenation of Earth's surface is equivocal. Iron could have consumed molecular oxygen when Fe³⁺-oxyhydroxides formed in the oceans, or it could have promoted atmospheric oxidation by means of pyrite burial. Through high-precision iron isotopic measurements of Archean-Paleoproterozoic sediments and laboratory grown pyrites, we show that the triple iron isotopic composition of Neoarchean-Paleoproterozoic pyrites requires both extensive marine iron oxidation and sulfide-limited pyritization. Using an isotopic fractionation model informed by these data, we constrain the relative sizes of sedimentary Fe³⁺-oxyhydroxide and pyrite sinks for Neoarchean marine iron. We show that pyrite burial could have resulted in molecular oxygen export exceeding local Fe²⁺ oxidation sinks, thereby contributing to early episodes of transient oxygenation of Archean surface environments.

44 Main Text

45 Irreversible changes to oxic and euxinic sedimentary iron sinks during the Archean and
46 Paleoproterozoic were intimately linked with the oxygenation of Earth's atmosphere during the
47 Great Oxygenation Event (GOE) beginning *ca.* 2.43 Ga (1, 2). Early oxygenation coincided with
48 enhanced sedimentary burial of iron sulfide (pyrite) driven by the greater availability of sulfate (3–
49 5). Through the pyrite iron sink, enhanced volcanic SO₂ fluxes in the Neoproterozoic could have
50 indirectly induced the release of oxygen via the microbial reduction of volcanically-derived sulfate
51 and the sequestration of sulfide in sedimentary pyrite (6–8). Meanwhile, iron could have acted as
52 a net sink of oxygen produced during oxygenic photosynthesis, if Fe²⁺ dissolved in the oceans was
53 not sequestered in sediments as pyrite, but rather as Fe³⁺-oxyhydroxides. It is presently unknown
54 if the balance of iron oxyhydroxide and pyrite sinks in certain marine sediments resulted in the net
55 production or removal of oxygen in the period leading to the GOE.

56 Sedimentary Fe isotopic records show large shifts across the GOE (9, 10) (Fig. 1A), and reflect
57 evolution of the Fe, S, and O cycles through the Archean and Paleoproterozoic (11). Pre-GOE
58 pyrites can have ⁵⁶Fe/⁵⁴Fe ratios shifted by up to -3.5‰ relative to most terrestrial rocks, a degree
59 of fractionation rarely seen in the post-GOE rock record (9). The interpretation of these pyrite Fe
60 isotopic compositions is not straightforward, because they could be controlled by (i) the size of
61 oxidizing iron sinks that removed isotopically heavy Fe³⁺-oxyhydroxides, leaving an isotopically
62 light dissolved Fe²⁺ pool from which pyrite formed (9, 10); (ii) microbial dissimilatory Fe³⁺
63 reduction (DIR) that preferentially releases an isotopically light Fe²⁺ pool (12, 13); and (iii) a
64 kinetic isotope effect (KIE) accompanying partial pyrite precipitation, which produces isotopically
65 light pyrite (14, 15). The relative importance of these processes remains debated (9–18), and this
66 uncertainty has hindered quantitative interpretation of the ancient iron cycle, exemplified by the
67 fact that Fe isotope records have not yet constrained the degree to which Fe removal on highly
68 productive continental margins was a net sink or source for early O₂ (8).

69 Here, we report triple-Fe-isotopic ratio measurements that allow us to remove ambiguities in
70 interpretations of the pre-GOE iron cycle. This approach relies on our discovery that the main
71 isotopic fractionation processes implicated in the formation of pre-GOE pyrites follow distinct
72 isotopic mass fractionation laws (MFLs), which describe how different isotopic ratios of the same
73 element covary (19, 20). To resolve MFLs, measurement of Fe isotopic ratios must be at higher
74 precision than is typically reported in analysis of ancient sediments. This approach has been used

75 in igneous geochemistry to show that Fe isotopic variations in magmatic olivine followed a kinetic
 76 MFL for diffusive transport (21), and in aqueous UV photo-oxidation experiments to investigate
 77 pathways to the deposition of iron formations (IF) (22). Measurements of this type, to a comparable
 78 or higher precision, are used more frequently in cosmochemistry to resolve nucleosynthetic
 79 anomalies in meteorite samples (23–26). For a given MFL, the ratio of $^{56}\text{Fe}/^{54}\text{Fe}$ to that of $^{57}\text{Fe}/^{54}\text{Fe}$
 80 defines the slope

$$81 \quad \theta^{56/57} = \Delta\delta^{56}\text{Fe}/\Delta\delta^{57}\text{Fe}, \quad (\text{Eq. 1})$$

82 where $\Delta\delta^x\text{Fe}$ is a change in $\delta^x\text{Fe}$; where $\delta^x\text{Fe}$ (‰) = $1000 \ln[(^x\text{Fe}/^{54}\text{Fe})_{\text{sample}}/(^x\text{Fe}/^{54}\text{Fe})_{\text{IRMM-014}}]$;
 83 imparted by physical, chemical, or biological processes. The $\Delta\delta^x\text{Fe}$ for natural samples is taken
 84 as the difference from the bulk silicate Earth, which is approximated by IRMM-014 (20, 22, 23,
 85 26). As discussed below, we also ran pyrite synthesis experiments and there the $\Delta\delta^x\text{Fe}$ value is
 86 taken as the difference from the starting material for each experiment. Isotopic trends following
 87 an array of MFLs are by definition mass-dependent. Apparent departures ($\epsilon^{56}\text{Fe}$) from an arbitrary
 88 reference MFL (20, 23, 27), which we choose here to be the high-temperature equilibrium limit
 89 law with $\theta^{56/57} = (1/53.939 - 1/55.935)/(1/53.939 - 1/56.935) = 0.678$, are defined as,

$$90 \quad \epsilon^{56}\text{Fe} = (\Delta\delta^{56}\text{Fe} - 0.678 \times \Delta\delta^{57}\text{Fe}) \times 10. \quad (\text{Eq. 2})$$

91 In $\epsilon^{56}\text{Fe}$ vs. $\Delta\delta^{57}\text{Fe}$ space, MFLs form straight lines whose slopes can be related to $\theta^{56/57}$
 92 through,

$$93 \quad \epsilon^{56}\text{Fe} = 10 \times (\theta^{56/57} - 0.678) \times \Delta\delta^{57}\text{Fe}. \quad (\text{Eq. 3})$$

94 In order to establish the values of $\theta^{56/57}$ corresponding to two end-member hypotheses that
 95 have been put forward to explain the $\delta^{56}\text{Fe}$ pyrite record (9, 10, 14), we measured:

96 (i) A suite of IF samples that show a large range in $\delta^{56}\text{Fe}$ values, including low $\delta^{56}\text{Fe}$ values
 97 that most likely reflect precipitation from an iron pool that had experienced extensive iron
 98 oxidation (28) (Table S1). These samples are well-suited to characterize the MFL expected if
 99 sedimentary pyrite formed from a distilled pool of Fe^{2+} enriched in light Fe isotopes (low $\delta^{56}\text{Fe}$)
 100 by precipitation of heavy (high $\delta^{56}\text{Fe}$) Fe^{3+} -oxyhydroxides.

101 (ii) Experimental products of pyrite synthesis via the $\text{FeS-H}_2\text{S}$ pathway (Fig. S2, Table S2),
 102 which produced pyrite that is isotopically lighter by as much as -2.4‰ in $\delta^{56}\text{Fe}$ relative to the
 103 initial FeS pool (Fig. S2) (27). In these experiments, we precipitated pyrite in anoxic conditions
 104 from an FeS precursor (27) following previously established protocols (14, 27, 29). The
 105 experiment yielded a pyrite precipitate and a residual FeS phase that were separated using a

106 calibrated sequential extraction (14), enabling us to measure the isotopic fractionation between the
107 reactant and product (Fig. S2). This fractionation represents a unidirectional KIE associated with
108 pyrite precipitation, because once formed pyrite is highly insoluble and does not readily exchange
109 with iron in solution. These pyrite samples represent a cumulative product reservoir rather than an
110 instantaneous precipitate, but any deviations from an intrinsic Fe isotope MFL caused by
111 cumulative effects are unresolvable within analytical uncertainties (27). Therefore, these
112 experimental run products are well suited to characterize the MFL expected if sedimentary pyrite
113 formation imparted a KIE on Fe isotopes.

114 The IFs, which were formed in the oceans after varying degrees of partial Fe²⁺ oxidation,
115 define a slope of $\theta^{56/57}_{ox}=0.6779\pm 0.0006$ for the oxidizing iron sink (here and elsewhere, the error
116 bars are 95% confidence intervals), which agrees with iron photo-oxidation experiments (22) and
117 is consistent with the view that equilibrium isotope exchange dominates during Fe²⁺ oxidation (20,
118 22). The pyrite-precipitation experiments involving a KIE gave $\theta^{56/57}_{KIE}=0.6743\pm 0.0005$.
119 Triple-Fe-isotopic slopes for the two end-member scenarios are measurably distinct (Fig. 1B).
120 Thus, we can use these slopes to address what caused Fe isotopic variations in pre-GOE
121 sedimentary pyrites.

122 We analyzed a suite of pre-GOE Neoproterozoic (2.66-2.32 Ga) pyrites with
123 depleted $\delta^{56}Fe$ values (as low as -3.1‰) and four black shales from the same formations (Fig. 1A,
124 Table S1). The pyrites and shales fall in an intermediate space on the triple-Fe-isotopic diagram
125 between the endmember MFLs for Fe oxidation and pyrite precipitation (Fig. 1B). We do not
126 interpret this data array as following a single MFL, because the pyrite and shale samples come
127 from several distinct formations and each sample requires contributions from more than one
128 fractionation process (with distinct MFLs). More likely, pre-GOE pyrite and shale $\delta^{56}Fe$ values
129 record a two-step process; partial marine Fe²⁺ oxidation during upwelling of Fe²⁺-rich deep waters
130 (9), and subsequent kinetic fractionation during partial, sulfide-limited pyrite formation from the
131 remaining Fe²⁺ reservoir (14, 15, 30). In this model, Fe-oxyhydroxide and pyrite sinks sequestered
132 iron upwelling from deep oceans lacking a discrete redoxcline that allowed progressive partial Fe²⁺
133 oxidation, towards black shale depositional settings (Figs. 2A, S7) (10, 27, 31). The loss of such
134 depleted $\delta^{56}Fe_{py}$ values after the GOE, which incidentally would prevent us resolving of MFLs
135 for younger samples, indicates that prevailing conditions of sulfide-limitation, and progressive

136 partial Fe oxidation, were diminished following biogeochemical overturn taking place from 2.32
137 Ga (11).

138 The pyrite samples that we analyzed are nodular, deforming sedimentary laminations around
139 them, and must have formed in the sediment during early diagenesis. They most likely inherited
140 their Fe isotopic compositions from pyrite precipitated in porewater near the sediment-seawater
141 interface, but in some cases dissolution-reprecipitation has eradicated their primary textural
142 features and caused recrystallization into massive forms. *In situ* work on Archean pyrites suggests
143 that these secondary texture-altering processes do not eradicate primary sedimentary Fe isotopic
144 signatures (18). A major source of iron to porewaters would have been downward diffusion of
145 overlying Fe²⁺-rich seawater into the sediments (9). The crux of the debate is whether pyrite simply
146 inherited the Fe isotopic composition of seawater, which was by far the largest exchangeable Fe
147 reservoir, or whether some kinetic isotopic fractionation was expressed, if pyritization was
148 incomplete due to limited sulfide supply. The new triple-Fe-isotopic measurements reported here
149 indicate that the latter case was true for the low $\delta^{56}\text{Fe}$ pre-GOE pyrites we studied.

150 For any isotopically light pyrite sample, we can estimate contributions to the $\delta^{56}\text{Fe}$ value from
151 prior oxidation of the Fe²⁺ pool, and the KIE during pyritization. To do so, we first calculate
152 contributions of Fe-oxidation to $\delta^{56}\text{Fe}$ values of the water mass ($\delta^{56}\text{Fe}_w$) from which pyrite
153 formed, from intercepts of the kinetic pyritization MFL passing through individual datapoints with
154 the oxidation MFL (Fig. 2B). We then determine the Fe isotopic fractionation imparted by
155 pyritization by taking the difference in $\delta^{56}\text{Fe}$ values between those of pyrite and $\delta^{56}\text{Fe}_w$ (Figs. 2B,
156 S5) (27).

157 Our approach assumes that partial iron oxidation and pyritization were the main drivers of
158 $\delta^{56}\text{Fe}$ variations in sedimentary pyrite. It is however conceivable that some porewater or marine
159 Fe²⁺ was sourced from DIR (12, 13, 32), a microbial metabolism that seems to have been active
160 since at least 3.2 Ga (18). This represents a source of uncertainty in our model. Experiments to
161 date suggest that the isotopic fractionation during DIR reflects equilibration of Fe²⁺ and Fe³⁺ after
162 the reduction step (33), and therefore we expect that it would fall into the same class of redox
163 equilibrium processes that define the Fe²⁺ oxidation MFL. The observed departure of natural pyrite
164 from this MFL therefore implies that regardless of the potential role of DIR, a KIE during
165 pyritization is also required to explain pre-GOE $\delta^{56}\text{Fe}_{\text{py}}$ values.

166 The fraction of Fe³⁺-oxyhydroxide removed to give the $\delta^{56}\text{Fe}_w$ value on the intercept ($F_{\text{ox}} = \text{Fe}$
167 in oxyhydroxide sink/total Fe sink), and the fraction of pyrite removed from that remaining Fe²⁺
168 pool ($f_{\text{py}} = \text{Fe in pyrite}/\text{Fe remaining after Fe removal to the oxyhydroxide sink}$), were calculated
169 under Rayleigh fractionation conditions (Figs. 2, S5; Table S5). The setting that we envision is
170 progressive Fe²⁺ oxidation as Fe²⁺-rich deep-waters are upwelled towards more oxidizing photic
171 zone conditions (9, 10) (Fig., S7). We also explored a 1-D dispersion-reaction steady-state model
172 for water-column Fe²⁺ oxidation, and find that our conclusions using Rayleigh distillation are
173 robust (27, 34). We treated pyrite as a cumulative product of pyritization (27). The fractional pyrite
174 sink, F_{py} , for iron in the whole depositional system is $F_{\text{py}} = f_{\text{py}} \times (1 - F_{\text{ox}})$. In Fig. 2D, we plot contours
175 of constant $F_{\text{ox}}/F_{\text{py}}$, showing that $\epsilon^{56}\text{Fe}$ measurements are diagnostic of the relative size of the
176 oxide and pyrite iron sinks.

177 To fully propagate the effect of uncertainties in sample measurements and $\theta^{56/57}$ values for the
178 end-member processes on uncertainties in F_{ox} , f_{py} , and F_{py} , we used a Monte-Carlo simulation (Fig.
179 3). Estimates for F_{py} span 10 to 80 % of the upwelled iron pool (within 95 % confidence interval)
180 for the low $\delta^{56}\text{Fe}$ pyrites that we studied. With initial pre-GOE deep-water $[\text{Fe}^{2+}]$ concentration
181 $\sim 50 \mu\text{M}$ (1), the pyrite sink could have removed 5 to 40 μM of dissolved iron. This requires ~ 10
182 to 80 μM of seawater-dissolved sulfate to be microbially reduced to sulfide, ~ 350 to 1,400 times
183 less than the modern seawater sulfate concentration of 28 mM, but within recent estimates for
184 Archean seawater sulfate based on S isotope modelling (35, 36). For the ~ 2.65 Ga Jeerinah and
185 Lokammona formations, we infer that as little as 10% of iron upwelled onto the shelf was deposited
186 as pyrite (Figs. 2C, 3, S6) (27).

187 When volcanic SO₂ is the primary sulfur source, burial of reduced sulfur in pyrite represents
188 a net oxidation of Earth's surface (6–8) (Fig. 2A). For example, the reaction $2\text{SO}_2 + \text{H}_2\text{O} + \text{Fe}^{2+}$
189 $\rightarrow \text{FeS}_2 + 2\text{H}^+ + 2.5\text{O}_2$; describing the net effect of SO₂ photolysis and hydrolysis, cyanobacterial
190 photosynthesis, microbial sulfate reduction, and pyrite precipitation; indicates that pyrite burial
191 can indirectly drive net O₂ export to the atmosphere-ocean system (8). The reaction provides a
192 maximum estimate for O₂ export during pyrite burial because: (i) a more reduced original sulfur
193 source would weaken the net oxidative effect of pyrite burial, and (ii) other types of primary
194 productivity, such as anoxygenic photoferrotrophy, which oxidizes Fe²⁺ directly, could have
195 contributed organic matter for sulfate reduction, but only cyanobacterial activity would have

196 produced O₂. A more realistic estimate for the volcanic H₂S/SO₂ emission ratio at ~1 (7) would
197 result in a net 1 mole O₂ yield per mole of pyrite buried.

198 To oxygenate the atmosphere via pyrite burial, the produced O₂ would also need to overcome
199 O₂ buffers in the ocean, primarily the upwelled Fe²⁺ flux (Fig. 2A). Oxygen-driven Fe²⁺ oxidation
200 consumes 0.25 moles of O₂ per mole of Fe³⁺ buried, so net O₂ sources and sinks will be balanced
201 when F_{ox}/F_{py} is 4 and 10 for volcanic H₂S/SO₂ emission ratios of 1 (7) and 0 (8), respectively.
202 Depending on F_{ox}/F_{py} ratios, iron deposition on productive continental margins could have been a
203 net source or sink for O₂ in the atmosphere-ocean system. Triple-Fe-isotopic systematics are
204 diagnostic of F_{ox}/F_{py} ratios (Fig. 2D). Pre-GOE pyrite data all fall above the F_{ox}/F_{py}=4 contour, and
205 the F_{ox}/F_{py}=10 contour is outside of the error bar on pyrite ε⁵⁶Fe values. We can therefore rule out
206 net O₂ sink-like behavior for the case where SO₂ dominated Neoproterozoic volcanic emissions. Even
207 with a conservative volcanic H₂S/SO₂ ratio of 1 (7), our data support a net O₂ source in Neoproterozoic
208 pyrite-forming environments, particularly after 2.52 Ga (Figs. 2D, 3). The inference that the oxic
209 sink did not overwhelm local oxygen sources associated with pyrite deposition also holds if F_{ox} is
210 calculated using a 1-D dispersion-reaction model (27, 34). Average results from Monte Carlo
211 simulations imply that even in the cases where we find the smallest F_{py} and largest F_{ox}, in ~2.65
212 Ga Jeerinah and Lokamonna formation pyrites, some O₂ could have been exported to the
213 atmosphere-ocean system during pyrite burial after exhausting local Fe²⁺ oxidation sinks. We
214 focused on the lowest δ⁵⁶Fe pyrites because these give us the most leverage to characterize MFLs.
215 Pre-GOE pyrites, while displaying much more negative δ⁵⁶Fe values (average of about -2 ‰) than
216 post-GOE pyrites (Fig. 1A), span a range of values. The more typical pyrites could have formed
217 from a seawater reservoir that did not experience such protracted Fe²⁺ oxidation (9, 10) or may
218 reflect higher degrees of pyritization. The amount of oxygen produced in such settings (moles of
219 O₂ generated per mole of pyrite buried) would have been higher than the values calculated here
220 for the isotopically lightest pyrites. The conclusion that iron oxide burial did not locally buffer O₂
221 generated by pyrite burial in the Neoproterozoic is therefore robust.

222 The triple-Fe-isotopic proxy provides new insights into the iron cycle in Earth's early oceans.
223 Before the GOE, large and probably fluctuating hydrothermal and riverine iron fluxes to the oceans
224 (31) were removed to two sedimentary sinks (Figs. 2A, S7) (27). The major sink was
225 Fe³⁺-oxyhydroxides that were deposited from upwelling water masses in the oceans that lacked a
226 discrete redoxcline and allowed protracted partial iron oxidation (9, 10). The second iron sink was

227 on highly productive continental margins, where deposition of pyrite-rich sediments was generally
228 sulfide-limited due to a small marine sulfate pool. Small relative changes in iron removal to these
229 oxyhydroxide and sulfide sinks potentially led to perturbations in the net O₂ supply to the
230 atmosphere-ocean system that fueled shallow-marine oxygen oases (37, 38) and helped prime the
231 Earth system for 'whiffs' of atmospheric O₂ in the runup to the GOE (39).

232

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422 isotopic compositions. AWH and ND performed modeling. All authors contributed to
423 interpretation of results. AWH, ND, and AB wrote the first draft of the manuscript, which was
424 subsequently edited with input from all authors.

425

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428

429 **Data availability:** All original data are reported in Tables in the Supplementary Online Materials.
430 Literature iron isotope data presented in Figure 1A are compiled in the EarthChem library at
431 <https://doi.org/10.1594/IEDA/111446>.

432

433 **List of Supplementary Materials:**

434 Materials and Methods

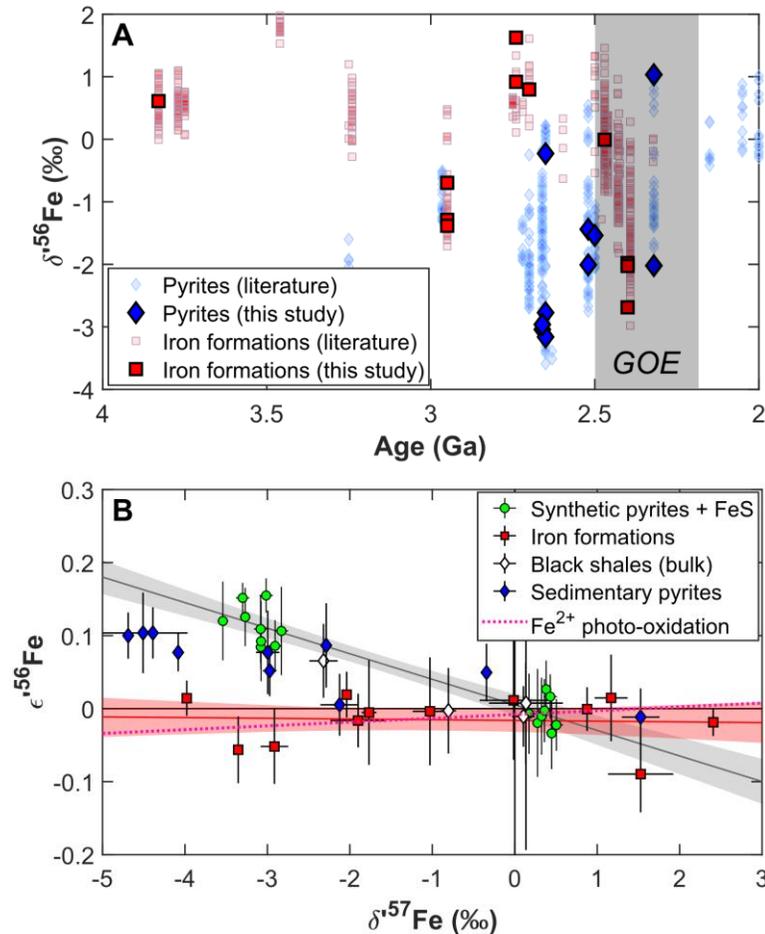
435 Supplementary Text

436 Figs. S1 to S10

437 Tables S1 to S5

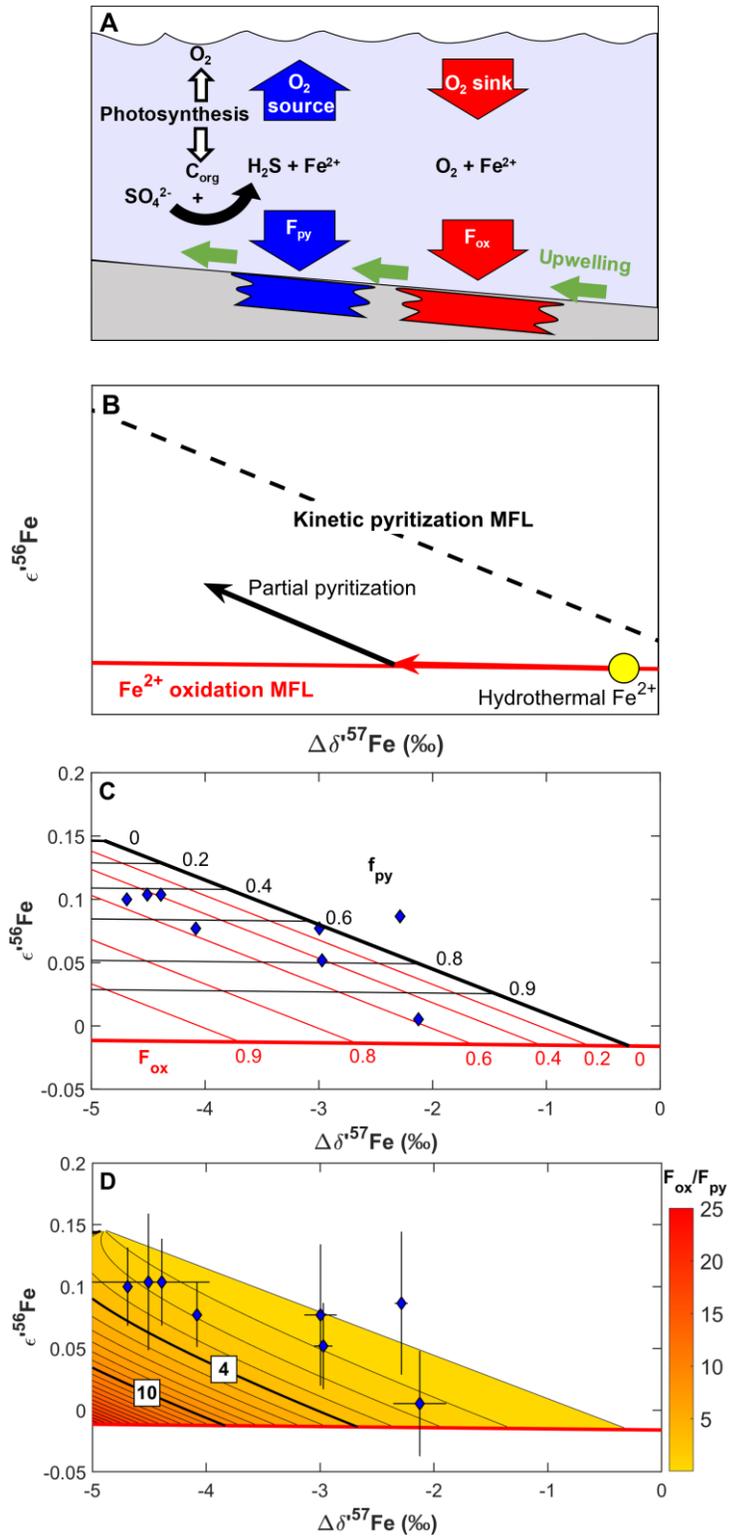
438 References 40-67

439

441 **Fig. 1.**

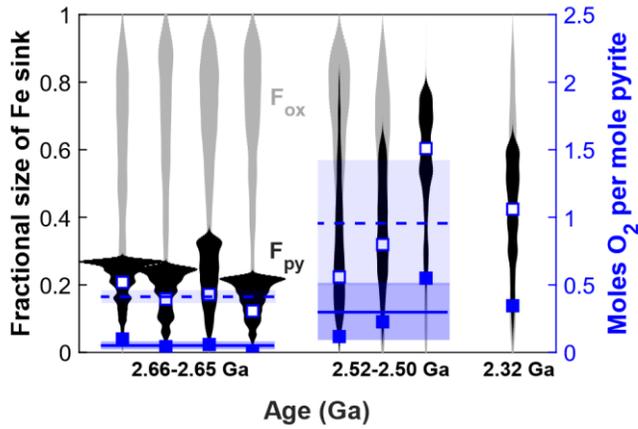
442 Iron isotope systematics of (i) pre-GOE sediments and natural pyrites, and (ii) synthetic pyrites
 443 and FeS produced in laboratory experiments (Tables S1, S2) (27). A. $\delta^{156}\text{Fe}$ (relative to IRMM-
 444 014) values of IFs and pyrites analyzed in this study, plotted against their age (published IF and
 445 pyrite data compiled in (11) are also plotted for reference). B. Triple-Fe-isotopic systematics for
 446 IFs, pyrites, and black shales in $\epsilon^{156}\text{Fe}$ vs. $\Delta\delta^{157}\text{Fe}$ space. $\Delta\delta^{157}\text{Fe}$ values are reported as differences
 447 from IRMM-014 and the starting material of experiments, for the natural samples and the synthetic
 448 pyrites, respectively. Error bars and envelopes are 95% confidence intervals. The slopes of end-
 449 member MFLs associated with iron-redox processes (red line and red envelope) and kinetic isotope
 450 effects (black line and grey envelope) during pyritization are constrained through analysis of
 451 isotopically light Mn-rich IFs and laboratory pyrite precipitated via the H_2S pathway (14, 27, 40),
 452 respectively. The slope of the IF MFL agrees well with the theoretical high-temperature
 453 equilibrium limit law (defined by the horizontal axis, (20)), and an experimentally determined

454 MFL for Fe^{2+} oxidation (via UV photo-oxidation (22)), implying control by Fe^{2+} - Fe^{3+} equilibrium.
455 Synthetic pyrite and FeS define a kinetic MFL for sulfide precipitation. Pre-GOE pyrites fall in an
456 intermediate space between redox-equilibrium and kinetic endmembers.



458 **Fig. 2.**

459 Interpretation of triple-Fe-isotope compositions of isotopically light pyrites. A. Schematic
460 representation of the Fe sinks (F_{ox} and F_{py}), and their inferred links to O_2 cycling in the pre-GOE
461 oceans. B. Triple Fe isotopic interpretation of the two-step process involved in pyrite formation.
462 Iron with starting composition resembling hydrothermal fluids (yellow circle; $\Delta\delta^{57}Fe = -0.3\%$
463 relative to IRMM-014 with $\epsilon^{56}Fe$ on the empirical MFL defined by IFs) is oxidized, driving
464 residual Fe^{2+} to lighter $\delta^{57}Fe$ compositions along the Fe^{2+} oxidation MFL. Partial pyrite
465 precipitation from this residual Fe^{2+} subsequently causes fractionation along the kinetic
466 pyritization MFL. The approach is detailed in Figure S5 with mathematical derivations provided
467 in Supplementary Materials (27). C. Pyrite data and contours for F_{ox} and f_{py} in triple-Fe-isotopic
468 space. Both Fe^{2+} oxidation and pyritization are modeled using Rayleigh distillations. Iron isotopic
469 fractionation during iron oxidation is assumed to reflect the composition of residual dissolved Fe^{2+}
470 experiencing fractional removal of Fe^{3+} -oxyhydroxide upon upwelling into oxidizing near surface
471 waters. Iron isotopic fractionation during pyritization is assumed to reflect the composition of the
472 cumulative product, as we analyzed relatively large pyrite nodules (27). The fraction of total
473 upwelled Fe deposited as pyrite is calculated as $F_{py} = f_{py} \times (1 - F_{ox})$. D. Pyrite data and contours
474 of F_{ox}/F_{py} (relative size of oxyhydroxide and pyrite sedimentary Fe sinks). Bold contours at 4 and
475 10 indicate thresholds for net O_2 source vs. sink behavior for volcanic H_2S/SO_2 inputs ratios of 1
476 (7) and 0 (8), respectively. In B.-D., $\Delta\delta^{57}Fe$ values are reported as differences from IRMM-014.
477



478 **Fig. 3.**

479 F_{ox} and F_{py} , and molar O_2 yield estimates from a Monte Carlo error propagation. Violin plots for
 480 probability densities of fractional size of Fe sink (grey: F_{ox} , black: F_{py}) determined from
 481 propagation of errors on the $\epsilon^{56}Fe$ and $\Delta\delta^{57}Fe$ values for each measured pyrite and the errors on
 482 the slopes of the MFLs (27). Blue filled and open squares: estimated molar O_2 yields per mole of
 483 pyrite buried for individual samples using H_2S/SO_2 input ratios of 1 (7) and 0 (8), respectively.
 484 Blue solid and dashed lines and shaded areas: mean molar O_2 yields for H_2S/SO_2 input ratios of 1
 485 (7) and 0 (8), respectively, and 95% confidence intervals for pyrites in two age bins.

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Supplementary Materials for

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Resolving the Role of Ocean Iron Sinks in Early Atmospheric Oxygenation

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502 Materials and Methods

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513 **Materials and Methods**

514 Methods

515 *Pyrite synthesis experiments*

516 To constrain the triple-Fe-isotopic expression of pyrite precipitation, we performed new
517 laboratory pyrite precipitation experiments in an anoxic environment. Pyrite was synthesized at
518 the University of Edinburgh, via the FeS-H₂S pathway following the methodology of Guilbaud et
519 al. (2011) (14) and references therein, which produces pyrite precipitates from an FeS_m
520 (mackinawite) reactant. We provide a brief overview here, and the detailed protocol is described
521 below. First, we produced a solid FeS_m precursor by combining equimolar solutions of Fe²⁺ and
522 sulfide. This solid reactant was filtered and freeze dried and then sealed into reaction vessels in a
523 pH buffer solution. The sealed reaction vessels were then attached to a gas-mixing manifold and
524 injected with a controlled volume of H₂S, which was generated by reacting sodium sulfide with
525 sulfuric acid. The vessels were resealed, and the pyrite precipitation reaction was allowed to
526 proceed for a few hours to a few days, after which pyrite and residual FeS were separated using a
527 calibrated chemical extraction technique (14). We measured the triple-Fe-isotopic fractionation
528 between FeS and pyrite, which has been shown previously to be the reaction where a large kinetic
529 isotope effect is imparted to pyrite (14).

530 All reagents were of analytical grade, and solutions were prepared using 18 MΩ/cm deionized
531 water and sparged for 30 min with O₂-free grade N₂ before use. Solutions were prepared and solid
532 FeS_m was synthesized in N₂-filled recirculating Saffron alpha anoxic chamber under O₂-free
533 conditions. FeS_m was precipitated by mixing 100 mL of 0.6 M iron (Fe²⁺) solution prepared with
534 Mohr's salt [(NH₄)₂Fe(SO₄)₂·6H₂O; Sigma Aldrich] with 100 mL of 0.6 M sulfide solution made
535 with Na₂S·9H₂O (Sigma Aldrich). This reaction produced a black precipitate. The precipitate was
536 filtered using a Buchner filter with Whatman™ No 1 filter paper, resuspended in sparged water
537 and the filtration was repeated three times. The freshly precipitated FeS_m was freeze-dried
538 overnight on a Mini-Lyotrap (LTE) freeze-dryer then transferred back to the anoxic chamber and
539 stored under O₂-free conditions until use. The low-metal complexing MOPS (3-(N-
540 morpholino)propanesulfonic acid, pK_a = 7.31, Fisher) buffer was made by dissolution of its
541 sodium salt in sparged water, buffered to pH 6 by NaOH titration. Redox buffer Ti³⁺ citrate,
542 required for poisoning the Eh during sample recovery, was prepared by adding 5 mL 15% TiCl₃ to
543 50 mL 0.2 M Na citrate and buffered to pH 7 with Na₂CO₃. The solutions were stored in the glove
544 box under O₂-free conditions until use.

545 The pyrite precipitation experiments were prepared in the glove box. Approximately 300 mg
546 of the freeze-dried FeS_m was weighed into serum bottles, 10 mL of 0.05 M MOPS buffer solution
547 was added, and the bottles were sealed with rubber stoppers and aluminum crimper seals. The
548 sealed bottles were attached to a gas transfer manifold via a hypodermic needle inserted through
549 the rubber stopper, and the manifold and reaction bottle were flushed with O₂-free grade N₂ and
550 pumped down to -14 PSI (-97 kPa) three times. A sealed serum bottle containing 800 mg solid
551 Na₂S·9H₂O was attached to the manifold via a hypodermic needle and flushed and pumped three
552 times. A syringe was used to inject 2 mL of sparged, 50 vol% H₂SO₄ into the Na₂S·9H₂O-
553 containing bottle to generate H₂S. After H₂S transfer into the FeS_m-containing serum bottle, N₂
554 was added until pressure in the serum bottle was at only slight under-pressure relative to
555 atmospheric pressure (~ -2.5 PSI or ~ -17 kPa). The needle holes in the serum bottle septa were
556 covered with silicone sealant and the bottles were transferred to an oven at 40°C to allow the pyrite
557 precipitation reaction to take place. After different, pre-determined reaction durations (between ~5

558 and 120 hours), the serum bottle reaction vessels were removed from the oven and frozen to stop
559 the reaction.

560 Once frozen, the serum bottles were unsealed under flushing N_2 and excess H_2S in the
561 headspace was removed. The bottles were then re-stoppered, the stoppers pierced with a
562 hypodermic needle under flushing N_2 , and the bottles left in the freeze-dryer for a day. The
563 freeze-dried serum bottles were transferred to the anoxic chamber, and 2 mL sparged water and a
564 few drops of the Ti^{3+} citrate were added to poise the Eh at low negative values to prevent FeS_m
565 oxidation and ensure full dissolution of FeS_m following a previously established preferential
566 dissolution protocol (14, 41). The serum bottles were resealed and moved to a fume hood for
567 preferential dissolution. In the fume hood, 20 mL of sparged 1.2 M HCl was injected into the
568 serum bottle via hypodermic syringe to fully dissolve only FeS_m and MOPS salt. Remaining solids,
569 essentially pyrite, were separated by filtering on a 0.45 μm Millipore filter, and rinsing with
570 sparged water. The FeS_m in HCl solutions were adjusted to 50 mL by addition of water and a 10
571 mL (20%) cut was dried down in clean Savillex Teflon beakers for transport and isotopic analysis.
572 Pyrite was dissolved with drops of concentrated HNO_3 , solutions were adjusted to 50 mL by
573 addition of water and a 10 mL (20%) cut was dried down in clean Savillex Teflon beakers for
574 transport and isotopic analysis. A 20 mL cut was taken for pyrite samples SB5 Py and SB6 Py,
575 which were produced over short (4.66 hours) duration experiments and for which low pyrite iron
576 yields were anticipated. In the Origins Laboratory at the University of Chicago, samples were
577 dissolved in Aqua Regia with drops of 11 M $HClO_4$ at 140°C, and dried down twice, then treated
578 three times with 2 mL of H_2O_2 to remove organic carbon salts left in the FeS_m solutions by MOPS.
579 The solutions were then re-dissolved in 5 mL 6 M HCl for iron purification. A small aliquot of
580 each solution was dried down and redissolved in 0.3 M HNO_3 to check for iron concentration of
581 these solutions using MC-ICP-MS and determine the correct amount of volume of each sample
582 solution to be passed through iron purification.

583 *Analytical methods*

584 Analytical procedures for iron purification and isotopic measurements followed standard
585 procedures used at the Origins Laboratory of The University of Chicago (22, 25, 26, 42, 43).
586 Samples were prepared from powders of black shale and IF materials, and hand-picked pyrite
587 grains. Sample masses ranged between 12-22, 2-6, and 13-84 mg for black shale, IF, and pyrite
588 grains, respectively. Samples were digested in clean Savillex Teflon beakers. First, 1 ml of 28 M
589 HF + 0.5 ml of 15 M HNO_3 + a few drops of 11 M $HClO_4$ was added, and closed beakers were
590 heated at 130°C. Samples were evaporated to dryness and re-dissolved in Aqua Regia (0.75 ml of
591 11 M HCl + 0.25 ml of 15 M HNO_3) and a few drops of 11 M $HClO_4$, before heating and
592 evaporation was repeated. The Aqua Regia + $HClO_4$ step was repeated 3 times to release all iron
593 to solution. Samples were evaporated to dryness and 0.5 ml of 6 M HCl or 10 M HCl was added,
594 depending on the purification procedure to be used. Larger volumes of the same acid were used
595 for digestion of pyrite grains, which contained greater masses of Fe. Iron purification made use of
596 both the standard 'short column' procedure, which is now routinely used in the Origins Laboratory
597 (42, 43), and a 'long column' procedure designed to more effectively eliminate Cu from the matrix
598 (25, 26), which was a potential concern for sulfide samples.

599 *Short-column iron purification:* Disposable Bio-Rad Poly-Prep polyethylene columns were
600 filled with 1 ml of AG1-X8 200-400 mesh Cl-form anion exchange resin. The resin was pre-
601 conditioned with 10 ml of MilliQ H_2O , 5 ml of 1 M HNO_3 , 10 ml of MilliQ H_2O , 9 ml of 0.4 M
602 HCl, 5 ml of MilliQ H_2O , and 2 ml of 6 N HCl. Samples were loaded onto columns in 0.25 ml of
603 6 M HCl. Matrix and interfering elements were eliminated by passing 8 ml of 6 M HCl through

604 the column. Iron was eluted with 9 ml of 0.4 M HCl and recovered in clean Teflon beakers.
 605 Samples were evaporated to dryness and re-dissolved in 0.25 ml of 6 M HCl, before repeating the
 606 column procedure a second time with new resin. All experimentally synthesized pyrite and FeS_m
 607 samples were also purified using this procedure.

608 *Long-column iron purification:* This alternative iron purification procedure was used to
 609 eliminate Cu as a potentially significant matrix element associated with natural sulfide phases.
 610 Reusable 30 ml Savillex Teflon columns with a 0.64 cm ID cut to 10.5 cm length were loaded with
 611 3 ml of AG1-X8 anion exchange resin. The resin was preconditioned with 10 ml of MilliQ H₂O,
 612 10 ml of 0.4 M HCl, 5 ml of MilliQ H₂O, 10 ml of 0.4 M HCl, and 4 ml of 10 M HCl. Samples
 613 were loaded onto columns in 0.25 ml of 10 M HCl. Matrix and interfering elements were
 614 eliminated by passing 4.5 ml of 10 M HCl, and 30 ml of 4 M HCl, the latter to eliminate Cu. Iron
 615 was eluted with 9 ml of 0.4 M HCl and recovered in clean Teflon beakers. Samples were
 616 evaporated to dryness and re-dissolved in 0.25 ml of 10 M HCl before repeating the column
 617 procedure with new resin.

618 Iron isotopic compositions were measured on a Neptune MC-ICPMS at the University of
 619 Chicago. Analyses were made of the extent of isotopic fractionation (δ' values), and the departure
 620 from a reference mass-dependent fractionation law (ϵ'). The Fe isotopes at masses 54, 56, 57, and
 621 58 were measured simultaneously along with ⁵³Cr and ⁶⁰Ni for correction of ⁵⁴Cr and ⁵⁸Ni
 622 interferences on ⁵⁴Fe and ⁵⁸Fe, respectively. The ⁵³Cr and ⁶⁰Ni interferences were corrected for
 623 using the exponential law. All the Fe isotopes have molecular interferences with argide ions
 624 (⁴⁰Ar¹⁴N⁺, ⁴⁰Ar¹⁶O⁺, ⁴⁰Ar¹⁶O¹H⁺, and ⁴⁰Ar¹⁸O⁺), which present a significant hindrance to obtaining
 625 the requisite precision to resolve mass-dependent fractionation laws. Therefore, measurements
 626 were made on the flat-topped peak shoulder in high-resolution mode using a standard Neptune
 627 entrance slit. A few analyses were done at ultra-high resolution using a Thermo Element 2 slit.
 628 Results were consistent with those obtained using the standard HR method, but offered no
 629 improvement in precision while requiring higher iron concentrations to obtain the same signal.
 630 Nickel or aluminum sampler and H skimmer cones were used. Standard-sample bracketing was
 631 used to correct isotopic ratio measurements for instrumental mass fractionation, and Fe isotopic
 632 ratios of samples are reported relative to the average isotopic ratios of the bracketing standard
 633 solutions of IRMM-524, which has an identical Fe isotopic composition to IRMM-014. The
 634 exponential law was initially used to calculate ϵ values by fixing ⁵⁷Fe/⁵⁴Fe_{std} to 0.362549, the value
 635 of IRMM-014. The δ and ϵ values of samples are given by:

$$636$$

$$637 \quad \delta = \left[\left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{sample}} / \left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{std}} - 1 \right] \times 10^3, \quad (\text{S1})$$

$$638 \quad \epsilon = \left[\left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{sample}}^* / \left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{std}}^* - 1 \right] \times 10^4, \quad (\text{S2})$$

639
 640 and the logarithmic forms, δ' and ϵ' , are given by:

$$641$$

$$642 \quad \delta' = \ln \left[\left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{sample}} / \left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{std}} \right] \times 10^3, \quad (\text{S3})$$

$$643 \quad \epsilon' = \ln \left[\left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{sample}}^* / \left(\text{}^i\text{Fe}/\text{}^{54}\text{Fe} \right)_{\text{std}}^* \right] \times 10^4, \quad (\text{S4})$$

644

645 where $i = 56, 57,$ or 58 and the $*$ indicates that ratios were corrected for mass fractionation by
 646 internal normalization to a fixed reference $^{57}\text{Fe}/^{54}\text{Fe}$ ratio using the exponential law (17, 20) with
 647 $\theta^{56/57} = \ln(m_{i\text{Fe}}/m_{54\text{Fe}}) / \ln(m_{56\text{Fe}}/m_{54\text{Fe}}) = 0.672$, using the following equation,
 648

$$649 \quad \ln(i\text{Fe}/^{54}\text{Fe})_{\text{sample, corrected}}^* = \ln(i\text{Fe}/^{54}\text{Fe})_{\text{sample, measured}} - \ln \frac{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{sample, measured}} \ln(m_{i\text{Fe}}/m_{54\text{Fe}})}{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{fixed reference}} \ln(m_{57\text{Fe}}/m_{54\text{Fe}})}.$$

650 (S5)

651
 652 Bracketing standards were also internally normalized using the same exponential law. The
 653 bracketing standards were solutions of IRMM-524, which has the same isotopic composition as
 654 IRMM-014.

655 Subsequent to measurements, data were renormalized to the high-temperature equilibrium
 656 limit law running through IRMM-014 with $\theta^{56/57} = 0.678$, for display on Figs. 1B, 2B, 2C, 2D, and
 657 S6, consistent with the common convention used with other isotopic systems (e.g. 21, 37, 38). The
 658 renormalization of ϵ'^{56} values was done using
 659

$$660 \quad \epsilon'_{\text{high-T eq}} = \epsilon'_{\text{exp}} - 10 \times (0.678 - 0.672) \times \Delta\delta'^{57}\text{Fe}.$$

661 (S6)

662 Both the data normalized to the exponential law and to the high-temperature equilibrium limit
 663 law are presented in Tables S1 and S2, and a version of Figure 1B using normalization to the
 664 exponential law is shown on Figure S1.

665 Samples and standards were measured in 0.3 M HNO_3 and introduced into the plasma torch
 666 using a Cetac Aridus II or ESI Apex Omega desolvating nebulizer system with no auxiliary N_2
 667 flow. On-peak zero was determined at the start of each measurement sequence by analyzing a clean
 668 aliquot of the same HNO_3 in which samples were measured. Sample and standard concentrations
 669 between 5 and 30 ppm were used in different measurement sessions depending on sensitivity and
 670 the mass-resolution slit being used, but most analyses made use of 10-12 ppm iron in sample and
 671 standard solutions. Measurements were made with the use of bracketing standards matched to
 672 sample concentrations within $\pm 5\%$. Measurements of ^{56}Fe were made on a $10^{10} \Omega$ amplifier
 673 resistor because signal intensities were generally higher than 50 V, and $10^{11} \Omega$ amplifier resistors
 674 were used for measurement of ^{54}Cr , ^{54}Fe , ^{57}Fe , ^{58}Fe , and ^{60}Ni .

675 For experimentally synthesized samples, the Fe isotopic fractionation ($\delta'^{56}\text{Fe}$) was also
 676 determined by standard Fe isotopic analytical methods. A quartz cyclonic spray chamber was used
 677 to introduce 1 ppm solutions into the Neptune operating in medium-resolution mode, resulting in
 678 a signal of ~ 7 V. Isotopic compositions were determined by standard-sample bracketing. All Fe
 679 isotopic analyses of experimentally synthesized samples (both triple isotopic and conventional)
 680 were bracketed and normalized to IRMM-524 during analysis. The average fractionation factor
 681 we determined for the pyrite precipitation reaction was $\alpha^{56}_{\text{FeS-pyrite}} = 1.0023 \pm 0.0003$ (95% C.I.)
 682 (Fig. S2), consistent with the results of Guilbaud et al. (2011) who obtained a value of $1.0022 \pm$
 683 0.0007 (14). This fractionation factor was determined by calculating the average difference
 684 between the FeS_m and pyrite splits from each serum bottle experiment. The degree of pyritization
 685 (the fraction of the total Fe in the pyrite pool) was calculated from the total iron masses in each
 686 split indicated by concentration measurements and known dilution factors. The low degree of
 687 pyritization values (maximum $\sim 14\%$) obtained in our experiments were not conducive to fitting
 688 the data to a Rayleigh distillation trend, however the difference between linear trends plotted

689 through $\delta^{56}\text{Fe}$ vs. degree of pyritization for the FeS_m and pyrite data also gave an average
 690 fractionation factor of $\alpha^{56}_{\text{FeS-pyrite}} = 1.0023$ (Fig. S2).

691 We saw no systematic difference between short- and long-column purification techniques in
 692 triple-Fe-isotopic data for IF sample JD-C165A, and pyrite sample SF-1 599.8 Py, which were
 693 each processed multiple times using either column procedure to check the reproducibility of our
 694 measurements in the absence of geostandard materials that have been analyzed to this level of
 695 precision (Fig. S3). In all cases, the individual analyses for the pyrite sample had $\epsilon^{56}\text{Fe}$ values that
 696 were significantly more positive than the value anticipated for IF with the same $\Delta\delta^{57}\text{Fe}$ value (Fig.
 697 S3). In addition, as a check for possible matrix effects in the preparation of IF and pyrite samples,
 698 we performed a matrix test with IRMM-524 standard iron solution. Briefly, aliquots of an IF
 699 sample (REX 187.5) and a pyrite sample (SF-1 623.6 Py) were passed through the short-column
 700 purification procedure and the eluted matrix from each was collected. These matrix cuts were
 701 further purified by passing them through this column chemistry procedure again. The matrix cuts
 702 were mixed with a solution of IRMM-524 containing the same amount of iron as originally present
 703 in the sample aliquots, and the iron was purified with two passes on short columns in the same
 704 manner as other samples. The $\epsilon^{56}\text{Fe}$ values of both matrix-adjusted solutions and a pure solution
 705 of IRMM-524 were all within error of zero and all identical within error (Fig. S3), suggesting that
 706 sample matrix did not systematically affect our $\epsilon^{56}\text{Fe}$ analyses.

707

708 *Modeling methods - Calculation of oxic and sulfidic sink sizes*

709 Triple-Fe-isotopic systematics allows the isotopic composition of any low- $\delta^{57}\text{Fe}$ pyrite to be
 710 broken into contributions from KIE during pyrite precipitation and the isotopic fractionation
 711 resulting from the removal of isotopically heavy Fe^{3+} oxyhydroxides. Because MFLs are straight
 712 lines in $\epsilon^{56}\text{Fe}$ vs. $\Delta\delta^{57}\text{Fe}$ space, the contributions of the two fractionating processes can be
 713 determined by solving for the intersection of two straight line equations (shown schematically in
 714 Fig. S5), or as shown below, by solving a pair of simultaneous equations.

715 For each individual pyrite, the two unknowns are the $\epsilon^{56}\text{Fe}$ value and the $\Delta\delta^{57}\text{Fe}$ of the Fe^{2+}
 716 pool from which pyrite formed ($\delta^{56}\text{Fe}_w$ in the main text). We denote these two unknowns $\epsilon^{56}\text{Fe}_w$
 717 and $\Delta\delta^{57}\text{Fe}_w$. In the context of the two-stage model described here and in the main text, we have
 718 the two following constraints: (1) the parcel of seawater that experienced iron oxide removal must
 719 be on the empirical MFL defined by iron formation, and (2) the line that ties a pyrite sample to
 720 the seawater parcel from which is formed must define a slope identical to the MFL for pyritization.
 721 The two equations relating $\epsilon^{56}\text{Fe}_w$ and $\Delta\delta^{57}\text{Fe}_w$ are:

722

$$723 \quad \epsilon^{56}\text{Fe}_w = a_{\text{ox}}\Delta\delta^{57}\text{Fe}_w + b_{\text{ox}}, \quad (\text{S7})$$

724

$$725 \quad \frac{\epsilon^{56}\text{Fe}_{\text{py}} - \epsilon^{56}\text{Fe}_w}{\Delta\delta^{57}\text{Fe}_{\text{py}} - \Delta\delta^{57}\text{Fe}_w} = a_{\text{KIE}}, \quad (\text{S8})$$

726

727 where a_{ox} , b_{ox} , and a_{KIE} are the known empirical values from our measurements of endmember
 728 MFLs, and $\Delta\delta^{57}\text{Fe}$ are taken as fractionations relative to IRMM-014. These two equations can be
 729 solved for the two unknowns and we have,

730

$$731 \quad \Delta\delta^{57}\text{Fe}_w = \frac{(\epsilon^{56}\text{Fe}_{\text{py}} - a_{\text{KIE}}\Delta\delta^{57}\text{Fe}_{\text{py}} - b_{\text{ox}})}{(a_{\text{ox}} - a_{\text{KIE}})}, \quad (\text{S9})$$

732

$$\epsilon^{56}\text{Fe}_w = a_{\text{ox}} \frac{(\epsilon^{56}\text{Fe}_{\text{py}} - a_{\text{KIE}}\Delta\delta^{57}\text{Fe}_{\text{py}} - b_{\text{ox}})}{(a_{\text{ox}} - a_{\text{KIE}})} + b_{\text{ox}}. \quad (\text{S10})$$

733

734 Note that $\Delta\delta^{57}\text{Fe}_w \sim 1.5 \times \Delta\delta^{56}\text{Fe}_w$ where $\delta^{56}\text{Fe}_w$ values are discussed in the main text. The
735 extent of Fe^{2+} oxidation (F_{ox}) to give a certain $\Delta\delta^{57}\text{Fe}_w$ was calculated using a Rayleigh distillation
736 model:

737

$$738 \quad \Delta\delta^{57}\text{Fe}_w = \Delta\delta^{57}\text{Fe}_i + 1000(\alpha - 1) \ln(1 - F_{\text{ox}}), \quad (\text{S11})$$

739

740 where α is the fractionation factor during Fe^{2+} oxidation and precipitation that gives a fractionation
741 $1000 \times (\alpha^{56} - 1) = 1\text{‰}$ [$(\alpha^{57} - 1) \sim 1.5 \times (\alpha^{56} - 1)$] during Fe^{3+} oxyhydroxide removal (16), the subscript i
742 denotes the starting $\Delta\delta^{57}\text{Fe}$ value for a hydrothermal Fe^{2+} source of approximately -0.3‰ (46),
743 assumed to be on the empirical MFL defined by iron formations.

744

745 The fraction of pyrite precipitated (f_{py} in the main text) was also determined with a Rayleigh
746 distillation model. In this case, the measured fractionation was taken to reflect the cumulative
747 product of pyrite precipitation from a dissolved Fe^{2+} reservoir with initial $\Delta\delta^{57}\text{Fe}$ value of
748 $\Delta\delta^{57}\text{Fe}_w$. This contrasts with how one might consider *in situ* measurements of individual nodule
749 layers, because those better approximate instantaneous precipitate compositions during the growth
750 of pyrite grains (17, 18). The magnitude of the KIE that was expressed in the product was
751 calculated as the difference between the product and initial reactant:

751

$$752 \quad \Delta\delta^{57}\text{Fe}_{\text{py}} - \Delta\delta^{57}\text{Fe}_w = \frac{(f_{\text{py}} - 1) \times 1000(\alpha^{57} - 1) \ln(1 - f_{\text{py}})}{f_{\text{py}}}, \quad (\text{S12})$$

753

754 where we assumed the maximum fractionation for pyrite precipitation (via FeS_m) from Fe^{2+} of
755 $1000 \times (\alpha^{56} - 1) = -3.1\text{‰}$ [$(\alpha^{57} - 1) \sim 1.5 \times (\alpha^{56} - 1)$] suggested by ref. (14). The value of f_{py} was
756 determined by solving this transcendental equation numerically. The fractional size of the sulfidic
757 sink, F_{py} , witnessed by each pyrite, was calculated as,

758

$$759 \quad F_{\text{py}} = f_{\text{py}} \times (1 - F_{\text{ox}}). \quad (\text{S13})$$

760

761 An uncertainty not considered in calculating f_{py} is the effect of isotopic exchange between
762 freshly precipitated pyrite and ambient Fe^{2+} . A recent experimental study (47) provided some
763 evidence that the growing surface of freshly precipitated microscopic pyrite grains may undergo
764 isotopic equilibration with the ambient Fe^{2+} pool. Because the anticipated equilibrium
765 fractionation factor for pyrite formation is large and positive (48), such a process could partially
766 offset large kinetic isotope effects enriching pyrite in light Fe isotopes, resulting in a smaller net
767 fractionation between pyrite and Fe^{2+} at a given F_{py} . In practice, however, isotopic re-equilibration
768 of pyrite has been observed only at elevated temperatures (80°C), and where the surface area to
769 volume ratio of microscopic pyrites allows this surface exchange effect to exert a significant
770 control on the bulk Fe isotopic composition. This process should become diminishingly important
771 at lower temperatures, as observed in experiments (14) and nature (15), and as pyrite grains grow
772 larger than $10\ \mu\text{m}$, and certainly as they reach macroscopic sizes like the diagenetic nodules studied
773 here. While the required kinetic data on pyrite growth and isotopic exchange rates are not currently
774 available to model this process accurately at appropriate low-temperature marine conditions, it is
775 unlikely that isotopic re-equilibration of pyrite was a major control on the bulk Fe isotopic
776 composition of diagenetic pyrites.

777 In practice, all the parameters $\epsilon^{56}\text{Fe}_{\text{py}}$, $\Delta\delta^{57}\text{Fe}_{\text{py}}$, a_{ox} , b_{ox} , and a_{KIE} have analytical uncertainties
778 associated with them. The effects of these errors on estimates of fractional iron sinks were
779 propagated using a Monte Carlo method implemented in MATLAB. For each pyrite and IF
780 datapoint, an array of simulated datapoints was generated by randomly sampling 1000 times from
781 a normal distribution defined by the reported 95 % C.I. of the measured $\epsilon^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values
782 (Table S1). From the 1000 sets of randomly generated IF datapoints, 1000 MFLs were generated
783 by linear regression to encompass the anticipated range of seawater Fe^{2+} evolutions in $\epsilon^{56}\text{Fe}$ vs.
784 $\Delta\delta^{57}\text{Fe}$ space that could be driven by Fe^{3+} oxyhydroxide precipitation. An array of 1000 values
785 for the kinetic slope was generated by randomly sampling 1000 times from a normal distribution
786 defined by the 95 % C.I. of the experimentally determined slope. We then solved the 1000 resulting
787 simultaneous equations 1000 times for the randomly generated datasets using the approach
788 described above. Certain output values from the random resampling had to be rejected, as they did
789 not allow for solving for F_{ox} and f_{py} values using the Rayleigh distillation equations. These cases
790 were where: (i) the required fractionation during pyritization ($\Delta\delta^{57}\text{Fe}_{\text{py}} - \Delta\delta^{57}\text{Fe}_{\text{w}}$) was larger in
791 magnitude than the maximum instantaneous fractionation for pyrite precipitation from Fe^{2+} (via
792 FeS_m) with $1000 \times (\alpha^{56} - 1) = -3.1\text{‰}$ [$(\alpha^{57} - 1) \sim 1.5 \times (\alpha^{56} - 1)$] (14); (ii) the randomly generated data
793 placed a pyrite datapoint below the IF line in $\epsilon^{56}\text{Fe}$ vs. $\Delta\delta^{57}\text{Fe}$ space, thus requiring a positive
794 $\Delta\delta^{57}\text{Fe}$ offset of the pyrite from the IF line; and (iii) where the randomly generated data required
795 an intercept between the IF and KIE lines at a $\Delta\delta^{57}\text{Fe}_{\text{w}}$ value more positive than the assumed
796 hydrothermal Fe^{2+} source $\Delta\delta^{57}\text{Fe}$ value of approximately -0.3‰ (46). The probability distributions
797 for F_{ox} and F_{py} from the Monte Carlo simulation are shown in Fig. 3 and Table S5, and we also
798 used central estimates of F_{ox} and F_{py} from the Monte Carlo simulations to calculate the O_2 yields
799 given in Fig. 3 and Table S5. Monte Carlo simulation estimates of f_{py} and F_{ox} for each pyrite sample
800 span a large range, but these variations are strongly correlated. This is because a more negative
801 estimate for the isotopic composition of seawater $\Delta\delta^{57}\text{Fe}_{\text{w}}$ (which implies a larger F_{ox}), gives a
802 smaller estimate for the fractionation during precipitation of pyrite from the oceanic iron pool
803 (which implies a larger f_{py}). These two effects have an opposite impact on the estimate of F_{py} ,
804 therefore, F_{py} estimates vary less than F_{ox} and f_{py} .

805 As an alternative to a Rayleigh distillation describing upward large scale advection of Fe^{2+} -
806 rich deep waters (e.g. 49–52), we also explored the possibility that the isotopic evolution of the
807 Fe^{2+} reservoir during removal of Fe^{3+} oxyhydroxides to the oxic Fe sink was controlled by steady-
808 state eddy diffusion of Fe^{2+} from deep waters, and O_2 from the photic zone, following the model
809 of Czaja *et al.* (2012) (34). We developed a model to replicate its salient features, using a finite
810 difference approach. In the model, a photic zone with a fixed O_2 level overlies a basin that contains
811 anoxic, Fe^{2+} -rich water at depth. Dissolved O_2 is transported downward, and Fe^{2+} upward, by eddy
812 diffusion, and $\text{Fe}(\text{OH})_3$ precipitates where these species meet, following second-order reaction
813 kinetics with temperature and salinity-dependent rates calculated after ref. (53). Precipitation rates
814 peak in a narrow reaction zone, around which both dissolved species' concentrations decrease to
815 near zero levels. Precipitated $\text{Fe}(\text{OH})_3$ is removed from the column with a first-order rate constant
816 of 0.79 day^{-1} . The Fe^{2+} oxidation reaction (which consumes Fe^{2+} and O_2) follows a second-order
817 kinetic rate law that is dependent on temperature, salinity, and pH. This parameter space was
818 explored extensively by ref. (34) and we simply followed their preferred input parameters in order
819 to replicate their model. In the model, the equilibrium fractionation for Fe^{2+} - Fe^{3+} isotopic exchange
820 was implemented by treating ^{56}Fe and ^{54}Fe as separate species and scaling the reaction rate
821 constants according to the relevant fractionation factor. No fractionation factor was applied to the
822 eddy diffusion process. In the model, the majority of Fe oxidation takes place within the narrow

823 reaction zone, and it is there that significant Fe isotopic fractionations are developed in the Fe²⁺
824 reservoir in a steady-state distillation process.

825 A list of input parameters for different model runs is provided in Table S4. For simplicity, in
826 contrast to (34), we employed a fixed concentration rather than a fixed production rate boundary
827 condition for O₂. The fixed concentration we chose matches the steady-state O₂ level at the base
828 of the photic zone in ref. (34)'s model. Our results (Fig. S8) replicate theirs, so this simplification
829 of the boundary condition does not affect the model output.

830 It can be shown with a simple scaling argument that the steady state reaction zone develops
831 at the location where eddy diffusive transport of O₂ downwards, and Fe²⁺ upwards, lead to
832 concentrations of O₂ and Fe²⁺ in a 1:4 ratio, the stoichiometry required for complete titration of
833 dissolved Fe²⁺ by O₂-mediated oxidation. Consider a water column with 5 levels: Level 1 – ocean
834 surface; Level 2, photic zone base; Level 3 – top of reaction zone; Level 4 – base of reaction zone;
835 and Level 5 – base of model basin (Fig. S8). The diffusive fluxes, J_{O₂} and J_{Fe²⁺}, are given
836 approximately by,

$$837 \quad J_{O_2} = D[O_2]_2/z_{2-3}, \quad (S14)$$

$$838 \quad J_{Fe^{2+}} = D[Fe^{2+}]_5/z_{5-4}, \quad (S15)$$

841 where D is the eddy diffusivity (0.1 cm²s⁻¹), and z_{i-j} is the depth difference between level i and
842 level j, and the subscripts on the concentrations indicate concentrations at the fixed boundary
843 conditions for O₂ at the top of of the model, and Fe²⁺ at the base of the model. In the reaction zone,
844 Fe²⁺ is quantitatively oxidized by O₂, in a 4:1 stoichiometry, which gives the approximation
845 J_{O₂} ≈ ¼ J_{Fe²⁺} at this depth. Rearranging for z₅₋₄ gives:

$$846 \quad z_{5-4} \approx (z_{2-3}[Fe^{2+}]_5)/(4[O_2]_2). \quad (S16)$$

847
848 Recognizing that z₅₋₂ = z₅₋₄ + z₂₋₃ for the case where the reaction zone is ultimately thin, and
849 substituting appropriately gives:

$$850 \quad z_{5-4} \approx z_{5-2}/(1+(4[O_2]_2/[Fe^{2+}]_5)), \quad (S17)$$

851
852 and thus, the depth of the reaction zone can be calculated. This depth level is plotted in Figure S8
853 and agrees well with the depth level in the numerical model where the peak in Fe(OH)₃ is located.
854 This comparison and the fact that we can reproduce the profiles calculated by ref. (34) validates
855 our numerical code.

856 In the dispersion reaction model, the calculation of F_{ox} is less straightforward than in the
857 Rayleigh distillation because there is no provision for Fe removal as pyrite. In the context of an
858 upward Fe²⁺ supply, F_{ox} at a given depth was calculated by integrating the steady-state Fe²⁺
859 oxidation rate from the bottom of the model upward to that depth, and dividing this value by the
860 Fe²⁺ oxidation rate integrated over the entire water column.

861 We plotted δ⁵⁶Fe_{Fe²⁺} vs. ln(1-F_{ox}) from this model in Fig. S9, for different values of the
862 fractionation factor between Fe²⁺ and Fe(OH)₃. A feature of these model runs is that a small, but
863 significant negative isotopic fractionation is imparted to δ⁵⁶Fe_{Fe²⁺} before it reaches the reaction
864 zone, whilst F_{ox} is still very close to zero. This fractionation can be understood as resulting from
865 diffusion. The Fe²⁺ input at the base of the model region has a fixed ⁵⁶Fe/⁵⁴Fe, but due to
866

869 preferential removal of ^{56}Fe in the reaction zone, the ratio of concentration gradients is fractionated
870 relative to the input $^{56}\text{Fe}/^{54}\text{Fe}$ ratio, with a relatively steeper concentration gradient for ^{56}Fe . As a
871 result, ^{56}Fe diffuses slightly faster into the reaction zone, leaving the column underlying the
872 reaction zone with a slightly lower $^{56}\text{Fe}/^{54}\text{Fe}$. This is expressed in the slightly negative $\delta^{56}\text{Fe}_{\text{Fe}^{2+}}$
873 already established at the base of the reaction zone before Fe^{2+} oxidation begins to dominate the
874 isotopic evolution.

875 Once within the reaction zone, $\delta^{56}\text{Fe}_{\text{Fe}^{2+}}$ evolves linearly versus $\ln(1-F_{\text{ox}})$, becoming
876 increasingly negative as F_{ox} increases, so this evolution is functionally very similar to a Rayleigh
877 distillation. However, for a given input isotopic fractionation factor α^{56} between Fe^{2+} and $\text{Fe}(\text{OH})_3$,
878 the slope of $\delta^{56}\text{Fe}_{\text{Fe}^{2+}}$ vs. $\ln(1-F_{\text{ox}})$ is $\sim 0.39 \times (\alpha^{56} - 1) \times 1000$, while an upwelling modelled using
879 a Rayleigh distillation would yield a correlation of slope $(\alpha^{56} - 1) \times 1000$. As such, reaching a given
880 negative value of $\delta^{56}\text{Fe}_{\text{Fe}^{2+}}$ would require a larger F_{ox} at the same value of α^{56} , or vice versa, in the
881 dispersion-reaction model versus a Rayleigh distillation. This effect is partially offset, particularly
882 at lower F_{ox} values, by the initial depletion in $\delta^{56}\text{Fe}_{\text{Fe}^{2+}}$ caused by eddy diffusion in the underlying
883 water column.

884 F_{ox} and $F_{\text{ox}}/F_{\text{py}}$ were recalculated using the evolution described by model outputs in order to
885 compare to results from the model using Rayleigh distillation (Fig. S10). Dispersion-reaction
886 modeling conducted with an input value for α^{56} of 1.001 as used in our Rayleigh model, or 1.004
887 as used in ref. (34). Using $\alpha^{56} = 1.001$ in the dispersion-reaction model gives higher F_{ox} values than
888 in our Rayleigh distillation modeling. All pyrite triple Fe isotope compositions still lie at
889 $F_{\text{ox}}/F_{\text{py}} < 10$ (allowing positive O_2 fluxes in certain scenarios) but the error bars would also allow
890 marginal cases with higher $F_{\text{ox}}/F_{\text{py}}$ (Fig. S10). However, the same model would require $[\text{Fe}^{2+}]$ to
891 be depleted by partial oxidation by a factor of several hundreds in order to explain the lowest
892 recorded $\delta^{56}\text{Fe}_{\text{IF}}$ values, and it is unclear whether such extreme Fe^{2+} depletions would still allow
893 the deposition of Fe-rich chemical sediments at all. This suggests that the use of such a small α^{56}
894 value might not be appropriate in the context of this model, and why the larger fractionation factor
895 was employed in previous iterations of the model (34). That larger fractionation factor yields low
896 $F_{\text{ox}}/F_{\text{py}}$ consistent with pyrite burial being a net oxygen source (Fig. S10).

897

898 Sample Materials

899 Geological setting and age constraints for shale-hosted pyrite are given by Rouxel et al.
900 (2005) (9). Ages and stratigraphic positions for all samples used in this study are provided in Table
901 S3. References to age constraints for pyrite and shale samples, and most IF samples, are provided
902 in refs. (9, 10, 30). Ages for the Hotazel Formation and Isua Supracrustal Belt IFs are from ref. (2)
903 and ref. (54), respectively, and the geologic setting and Fe isotopic systematics of these IF have
904 been discussed in the literature elsewhere (28, 55, 56).

905 Pyrite grains from organic-rich shales as well as a few whole-rock organic-rich shale and IF
906 samples were selected for this study. Pyrite grains and whole-rock shale samples were selected
907 from a set of drill core samples previously studied for Fe isotopic variations by refs. (9, 30). New
908 pyrite grains were picked at the University of Hawaii. The nature of these grains was described in
909 detail by ref. (6). Pyrite in organic-rich shales that were subsampled in our study occur as nodules
910 ~ 1 mm to 1 cm in diameter, with C-rich inclusions in variable amounts. The nodular pyrite either
911 had no internal texture, or was composed of concentrically laminated, fine-grained pyrite or bladed
912 pyrite crystals. Euhedral pyrite crystals commonly overgrew the outer part of the nodules. Shale
913 laminae typically bend around pyrite nodules, which supports interpretation of their origin as being
914 formed early on during diagenesis. Pyrite nodules often display complex features such as multiple-

915 growth bands or composite nodules formed by coalescence of several nodules. Dissolution and
 916 reprecipitation of early diagenetic sulfide crystals and nodules could have happened in some
 917 samples and likely resulted in formation of massive, pre-compactional pyrite, often characterized
 918 by euhedral grains free of C-rich inclusions.

919 Localized dissolution-reprecipitation is unlikely to have affected Fe-isotopic compositions of
 920 pyrites. In the large sets of samples analyzed per formation by ref. (9), strongly negative $\delta^{56}\text{Fe}$
 921 values were a consistent feature, and no relationship between Fe isotopic composition and the
 922 nature of individual pyrite grains was reported, which supports the notion that these are primary
 923 sedimentary signatures and not the results of later alteration of the host rocks. The fidelity of the
 924 pyrite Fe isotope record as an archive of primary sedimentary signatures was recently discussed
 925 by ref. (11). In brief, the resistance of this system to metamorphic overprinting due to the high
 926 abundance of Fe, low solubility of pyrite, and small size of Fe isotopic fractionations at
 927 metamorphic temperatures all make it unlikely that primary sedimentary Fe isotopic signatures
 928 have been compromised by secondary processes that may nonetheless have affected the texture of
 929 pyrite grains. It was recently demonstrated through *in situ* work that Archean pyrites that
 930 experienced late fluid circulation, which led to partial recrystallization and alteration of S isotopic
 931 systematics, did not modify the Fe isotopic composition (18), in line with our expectations outlined
 932 above.

933 **Supplementary Text**

934 Background on mass fractionation laws for Fe isotopes

935 *Instantaneous fractionations*

936 Numerous reaction pathways have been proposed to create the $>5\%$ $\delta^{56}\text{Fe}$ range in Archean
 937 IFs, shales, and pyrites. The extent of Fe isotopic fractionation is insufficient to discriminate
 938 between different scenarios for sedimentary iron cycling in the Archean oceans, because several
 939 fractionation processes can generate a large and indistinguishable range in delta values.
 940 Considering two isotopic ratios can resolve this ambiguity for sedimentary pyrite, because
 941 different processes impart isotopic fractionations that follow different slopes in $\delta^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$
 942 space corresponding to mass fractionation laws (MFL). Mass-dependent fractionation is described
 943 with a power law:

944

$$945 \quad \alpha_{A/B}^{56} = \alpha_{A/B}^{57} \theta^{56/57}, \quad (\text{S18})$$

946

947 where $\alpha_{A/B}^x$ are fractionation factors for isotope x between reservoirs A and B, and $^{56/57}\theta$ is the
 948 mass dependent exponent or slope in triple Fe isotope space (20). Natural processes imparting
 949 different slopes of MFLs in three-isotope diagrams have been identified for O (57–60), Mg (19,
 950 61), S (44, 62, 63), Ca (64), Ti (64), and Fe (21, 22), but this has yet to be investigated for Fe
 951 isotopes in sedimentary rocks with enough precision to resolve distinct slopes. The slope $\theta^{56/57}$ for
 952 the triple-Fe-isotopic diagram is given by:

953

$$954 \quad \theta^{56/57} = \frac{\Delta\delta'^{56}\text{Fe}}{\Delta\delta'^{57}\text{Fe}} = \frac{\ln\left[\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{sample}} / \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{std}}\right] - \ln\left[\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{initial}} / \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{std}}\right]}{\ln\left[\left(\frac{^{57}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{sample}} / \left(\frac{^{57}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{std}}\right] - \ln\left[\left(\frac{^{57}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{initial}} / \left(\frac{^{57}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{std}}\right]}, \quad (\text{S19})$$

955

956 where δ' is related to the standard δ notation by:

957
958
959

$$\delta' = 1000 \times \ln[(\delta/1000) + 1]. \quad (\text{S20})$$

960 Slopes vary only subtly between MFLs and therefore it is convenient for the purpose of
961 visualization to express one isotopic ratio in terms of its deviation from an arbitrary reference law
962 in parts per 10,000 by using ϵ' notation (20, 22) where:

963
964
965

$$\epsilon'^{56}\text{Fe} = (\Delta\delta'^{56}\text{Fe} - \theta_r^{56/57} \times \Delta\delta'^{57}\text{Fe}) \times 10. \quad (\text{S21})$$

966 In $\epsilon'^{56}\text{Fe}$ vs. $\Delta\delta'^{57}\text{Fe}$ diagram, MFLs are straight lines, and when the high-temperature
967 equilibrium limit law with $\theta_r^{56/57} = 0.678$ is used as the reference law, $\epsilon'^{56}\text{Fe}$ values are 0 if
968 fractionation follows the high-temperature equilibrium limit law. Other MFLs will then have
969 positive or negative slopes if $\theta^{56/57}$ is larger or smaller than 0.678, respectively.

970 These laws describe mass-dependent fractionation in a single-step process. This approach is
971 an oversimplification in cases where isotopes have been fractionated via several geochemical
972 pathways, or via Rayleigh distillation. These complications are well-documented in the more
973 mature field of triple O and S isotopes (44, 57, 59, 62, 63) but we show here that these concerns
974 are of diminished importance in application to low-temperature Fe isotope systematics. This is
975 because Rayleigh distillation produces trends in $\epsilon'^{56}\text{Fe}$ vs. $\Delta\delta'^{57}\text{Fe}$ space that are practically
976 indistinguishable from instantaneous MFLs over the natural range of Fe isotopic variations.

977

Rayleigh distillation

Reactant reservoir

980 In the case of Rayleigh distillation, closed-system evolution of a reactant reservoir (A) during
981 formation of a product (B) results in an observed slope in three-isotope space for A that is distinct
982 from the intrinsic slope of the instantaneous fractionation process (Fig. S4A) (25, 62). In this study,
983 the evolution of the reactant reservoir corresponds to the generation of an isotopically light Fe^{2+}
984 pool through the removal of an isotopically heavy Fe^{3+} -oxyhydroxide product. The evolution of
985 the reactant, written in δ' notation, is,

986

$$\delta'^x\text{Fe}_A = (\alpha^x - 1) \times \ln(^{54}f_A) \times 1000 + \delta'^x\text{Fe}_{A,i}, \quad (\text{S22})$$

988

989 where $\delta'^x\text{Fe}_{A,i}$ is the initial isotopic composition of the reactant, $\delta'^x\text{Fe}_A$ is the isotopic composition
990 of the reactant when a fraction f_A of the reactant A remains, and α^x is the isotopic fractionation
991 factor for isotope x in the reaction of A to form product B.

992 In three-isotope space, the isotopic composition of the reactant will evolve with an effective
993 slope, $\theta^{56/57}_{\text{eff}}$,

994

$$\theta^{56/57}_{\text{eff}} = \frac{\delta'^{56}\text{Fe}_A - \delta'^{56}\text{Fe}_{A,i}}{\delta'^{57}\text{Fe}_A - \delta'^{57}\text{Fe}_{A,i}} = \frac{(\alpha^{56} - 1) \times \ln(^{54}f_A)}{(\alpha^{57} - 1) \times \ln(^{54}f_A)} = \frac{\alpha^{57\theta^{56/57}_{\text{inst}} - 1}}{\alpha^{57} - 1}, \quad (\text{S23})$$

996

997 where $\theta^{56/57}_{\text{inst}}$ is the intrinsic slope for the instantaneous reaction.

998 Distinction between θ_{inst} and θ_{eff} is significant in the O and S isotope systems, where
999 fractionations and relative isotopic mass differences are large. In the case of Fe isotopes,
1000 specifically Rayleigh distillation of aqueous Fe^{2+} driven by oxidation and removal of Fe^{3+}

1001 minerals, the relevant values for $\theta^{56/57}_{inst}$ and α^{57} are 0.678 and on the order of 1.0015, respectively
 1002 (14). Using these values results in $\theta^{56/57}_{eff} \approx 0.6778$, which is smaller than the intrinsic slope by
 1003 only 0.0002 and not resolvable from the intrinsic slope for any naturally occurring range of
 1004 fractionations (Fig. S4A). A slightly different relation between the effective and intrinsic slopes
 1005 for UV photo-oxidation, with $\alpha^{56} = 1.0012$, previously gave the same result that the effective slope
 1006 for the evolving reactant reservoir was smaller than the instantaneous slope by just 0.0002, and
 1007 thus the two slopes were indistinguishable within current measurement uncertainties (22). These
 1008 calculations imply that theoretical, single-step MFLs are an appropriate approximation for the
 1009 evolution in triple-Fe-isotopic space of an Fe^{2+} reservoir affected by oxidation and removal of Fe^{3+}
 1010 products following a Rayleigh distillation.

1011
 1012 *Cumulative product reservoir*

1013 The cumulative product reservoir during Rayleigh distillation, which is how we treat the pyrite
 1014 precipitation along the kinetic MFL, also follows a trend in triple-Fe-isotope space that is distinct
 1015 from the instantaneous MFL, however in this case the evolution is not linear. The evolution of the
 1016 cumulative product B is:

1017
 1018
$$\delta^x Fe_B = \left({}^{54}f_B - 1 \right) \times \ln \left[\frac{\left(1 - {}^{54}f_B \right)}{{}^{54}f_B} \right] \times \left(\alpha^x - 1 \right) \times 1000 + \delta^x Fe_{A,i}, \quad (S24)$$

1019 where $\delta^x Fe_B$ is the isotopic composition of the cumulative product when a fraction $f_B (= 1 - f_A)$ of
 1020 the reactant has been consumed.

1021 Nie *et al.* (22) showed that as the cumulative product reservoir grows and the reactant pool is
 1022 consumed, the deviation of the cumulative product $\epsilon^{56}Fe$ value, $\epsilon^{56}Fe_{cumulative}$, relative to value
 1023 $\epsilon^{56}Fe_{inst}$ that is expected to fall on the instantaneous MFL at a given $\delta^{57}Fe$ value is:

1024
 1025
$$\epsilon^{56}Fe_{cumulative} - \epsilon^{56}Fe_{inst} = 10,000 \left[\left(\theta^{56/57}_{inst} - 1 \right) \times \ln \left(1 - {}^{54}f_A \right) + \ln \left(1 - {}^{54}f_A \right)^{\alpha^{56}} - \right.$$

 1026
$$\left. \theta^{56/57}_{inst} \times \ln \left(1 - {}^{54}f_A \left(\alpha^{56/1/\theta^{56/57}_{inst}} \right) \right) \right]. \quad (S25)$$

1027
 1028 Here, the relevant values for $\theta^{56/57}_{inst}$ and α^{56} are 0.6743 (derived from our triple-Fe-isotope
 1029 measurements) and 0.9969 (the largest proposed Fe isotopic fractionation during pyrite
 1030 precipitation from Fe^{2+} via FeS_m (14)), respectively. Inserting these values into S25 gives a non-
 1031 linear trend shown in Fig. S4B, where the maximum deviation of the cumulative product reservoir
 1032 from the instantaneous MFL is less than 0.01 $\epsilon^{56}Fe$ units, and thus well within typical analytical
 1033 errors of 0.05 (95 % C.I.). These calculations imply that theoretical, single-step MFLs are an
 1034 appropriate approximation for the evolution in triple-Fe-isotopic space of cumulative product
 1035 reservoir pyrite following a Rayleigh distillation.

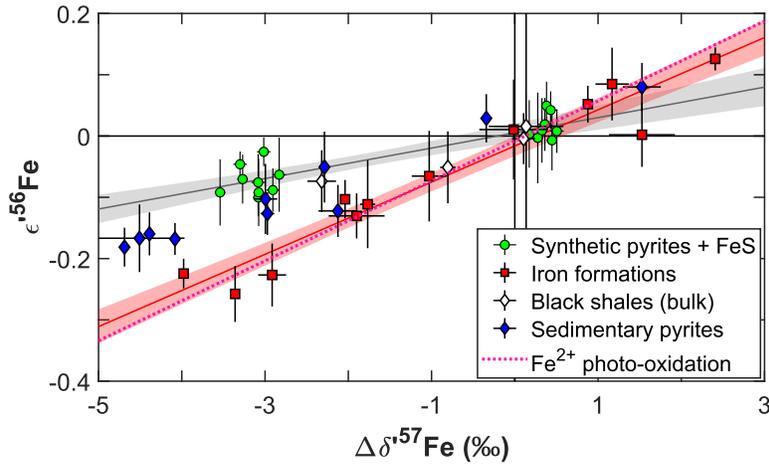
1036
 1037 *Iron isotope MFLs*

1038 Mass-dependent triple-Fe-isotopic systematics have been explored in few publications to
 1039 date, and only once previously in the context of low-temperature aqueous geochemistry. Nie *et al.*
 1040 (22) determined $\theta^{56/57} = 0.6785 \pm 0.0009$ associated with UV photo-oxidation of dissolved Fe^{2+} in

1041 anoxic solutions at near-neutral pH. A high precision measurement of the ca. 3.83 Ga IF-G
1042 geostandard from an IF in Isua, Greenland has $\epsilon^{56}\text{Fe}$ and $\Delta\delta^{57}\text{Fe}$ values consistent with
1043 isotopically heavy ferric precipitates from those experiments (22) and both are within error of the
1044 high-temperature limit equilibrium law with $\theta^{56/57} = 0.678$. However, the magnitude of isotopic
1045 enrichment in IF-G and isotopically heavy IF oxyhydroxides in general provide insufficient
1046 leverage in three-isotope space to distinguish different MFLs at the available precision for $\epsilon^{56}\text{Fe}$.
1047 Whether different iron oxidation pathways for IF deposition do have distinct MFLs has not yet
1048 been tested experimentally. However, the fact that the high-temperature equilibrium law, the MFL
1049 for photo-oxidation, and our observed MFL defined by IFs including the Hotazel Mn-rich IF
1050 samples that were most likely fractionated by direct O_2 oxidation (28), are all within error of one
1051 another, suggests that fractionations of Fe isotopes driven by Fe^{2+} - Fe^{2+} equilibration may follow
1052 the equilibrium MFL regardless of the oxidation process involved (66). The empirical constraints
1053 provided by new natural samples measurements here, and the experiments of Nie *et al.* (22), agree
1054 with the previously documented phenomenon that the high-temperature equilibrium limit law is
1055 broadly applicable in equilibrium isotope exchange processes including some of those that occur
1056 at low temperatures (20). The same may be true for Fe isotopic fractionation during iron reduction
1057 processes like DIR, as it has been shown that this process introduces fractionation during Fe^{2+} -
1058 Fe^{3+} equilibration following the reduction step (33). It will be important for future studies to
1059 constrain the value of $\theta^{56/57}$ for the remaining proposed oxidation pathway for IF, anoxygenic
1060 photoferrotrophy (51, 65). However our results to date suggest it is unlikely that triple-Fe-isotopic
1061 systematics will be able to identify the oxidation pathway for IF due to the tendency of Fe^{2+} and
1062 Fe^{3+} to rapidly isotopically equilibrate (66).

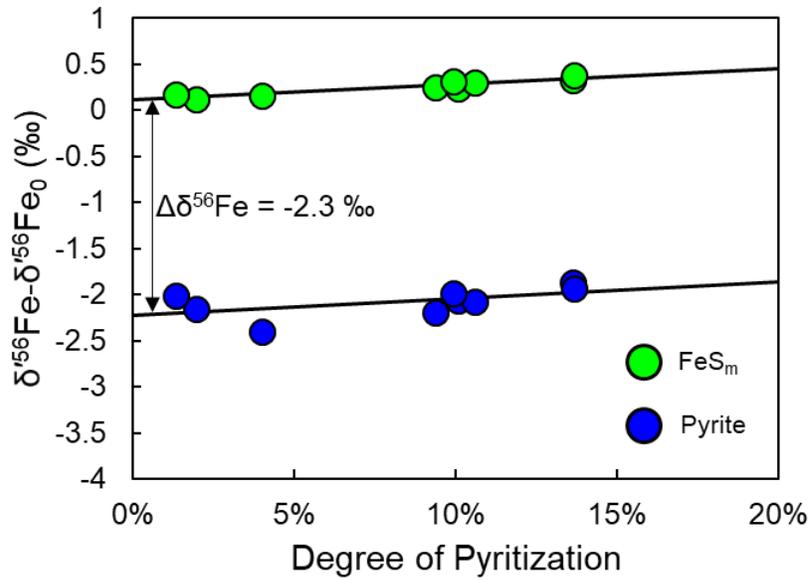
1063 Precipitation of pyrite is a kinetically controlled process associated with a large kinetic
1064 isotope effect that enriches early precipitates in the light isotopes of Fe (14, 15). The $\theta^{56/57}$ for
1065 kinetic processes can take a range of values depending on the specific reaction process taking
1066 place, but is in general expected to be smaller than the high-temperature equilibrium limit law
1067 $\theta^{56/57}$ value (19, 20). The value of $\theta^{56/57}$ relevant to pyrite precipitation did not have an empirical
1068 constraint prior to our study. Our pyrite precipitation experiments resulted in maximum degree of
1069 pyritization of ~14% (Fig. S2). By mass balance most iron was always left in the FeS_m pool and
1070 large fractionations from the starting composition of the experiment were observed in the pyrite
1071 pool, which provides leverage to determine the slope of the instantaneous MFL associated with
1072 pyrite precipitation. Our triple-Fe-isotopic analysis is consistent with a single kinetic MFL, with a
1073 slope $\theta^{56/57}_{\text{KIE}} = 0.6743 \pm 0.0005$. This is a much shallower slope than that of the equilibrium limit
1074 law associated with redox equilibrium (19, 20).

1075
1076



1079 **Fig. S1.**
1080

1081 Triple-Fe-isotopic systematics for IFs, pyrites, black shales, and laboratory grown pyrite and FeS,
1082 in $\epsilon^{56}\text{Fe}$ vs. $\Delta\delta^{57}\text{Fe}$ space, normalized to the exponential law (Tables S1, S2; Fig. 1A of the main
1083 text shows the same figure normalized to the high-T equilibrium MFL). $\Delta\delta^{57}\text{Fe}$ values are reported
1084 as differences from IRMM-014 and the starting material of experiments, for the natural samples
1085 and the synthetic pyrites, respectively. Error bars and envelopes are 95% confidence intervals. The
1086 slopes of end-member MFLs associated with iron-redox processes (red line and red envelope) and
1087 KIEs (black line and grey envelope) during pyritization are constrained through analysis of IFs
1088 and laboratory pyrite precipitates via the H_2S pathway (14, 27, 40), respectively. The slope of the
1089 IF MFL agrees well with the theoretical high temperature equilibrium limit law (defined by the
1090 horizontal axis, (20)), and an experimentally determined MFL for Fe^{2+} oxidation (via UV photo-
1091 oxidation (22)), implying control by Fe^{2+} - Fe^{3+} equilibrium. Synthetic pyrite and FeS define a
1092 kinetic MFL for sulfide precipitation. Pre-GOE pyrites fall in an intermediate space between
1093 redox-equilibrium and kinetic endmembers.
1094

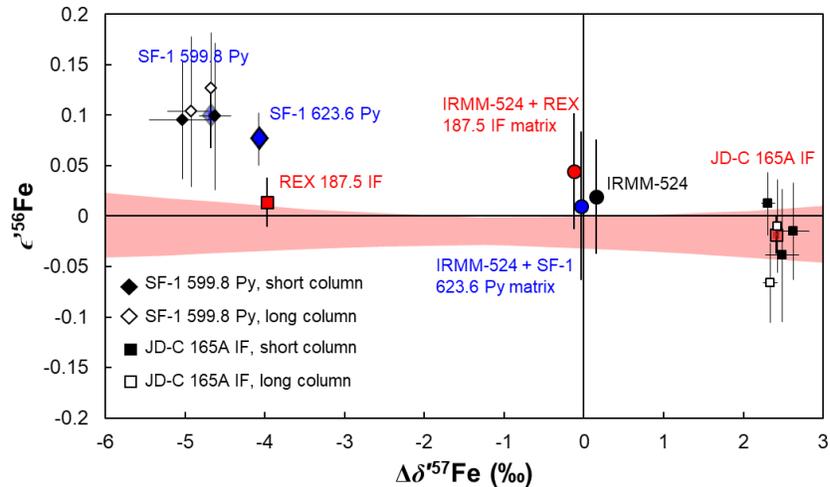


1095

1096 **Fig. S2.**

1097 Iron isotopic fractionation between FeS_m and pyrite during abiotic precipitation of pyrite. The
 1098 average Fe-isotopic fractionation between FeS_m and pyrite, a shift in $\delta^{56}\text{Fe}$ of -2.3 ‰, is
 1099 determined both through taking the average difference between the two phases in individual
 1100 experiments, and through the difference between linear fit lines of $\delta^{56}\text{Fe}$ vs. degree of pyritization.

1101

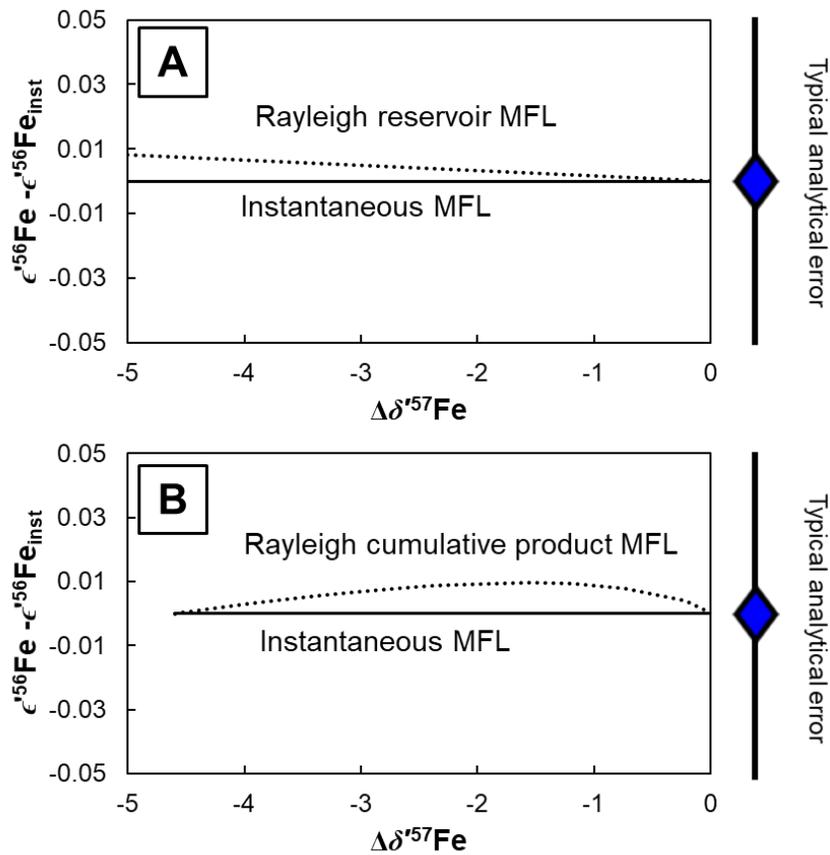


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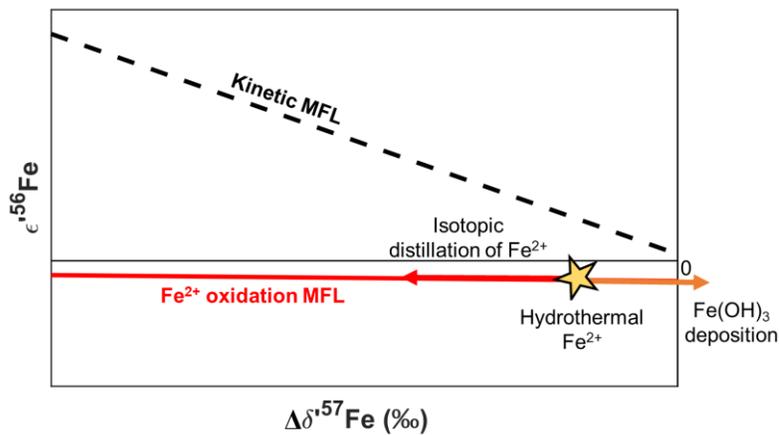
1103 **Fig. S3.**

1104 Tests performed on triple-Fe-isotopic analyses. Replicate aliquots of IF sample JD-C 165A and
 1105 pyrite sample SF-1 599.8, purified using short-column (black-filled symbols) and long-column
 1106 (open symbols) chromatography procedures were analyzed, with the average values for each
 1107 sample shown with the pale-colored symbols in the background. Despite some analytical scatter,
 1108 we see no significant or systematic effect of using one purification procedure over another, and all
 1109 replicate pyrite analyses were distinct from the triple-Fe-isotopic composition one would expect
 1110 for a sample that was fractionated solely by the redox processes driving the IF MFL (error
 1111 enveloped of the IF MFL is shaded in red). Matrix mixing tests were performed with IRMM-524
 1112 and matrix from IF sample REX 187.5 (bold, red square) and pyrite sample SF-1 623.6 Py (bold,
 1113 blue diamond). These revealed no resolvable matrix effect on $\epsilon^{56}\text{Fe}$ analysis, with the pure IRMM-
 1114 524 solution (black circle), IF matrix and IRMM-524 solution (red circle), and pyrite matrix and
 1115 IRMM-524 solution (blue circle) all having $\epsilon^{56}\text{Fe}$ values which are within error of one another
 1116 and zero. Note that if matrix effects drove the difference between pyrite and IF triple-Fe-isotope
 1117 variations, the IRMM-524 sample doped with pyrite matrix would have significantly more positive
 1118 $\epsilon^{56}\text{Fe}$ values than the IF-doped standard, which is not the case. $\Delta\delta^{57}\text{Fe}$ values are differences from
 1119 to IRMM-014.

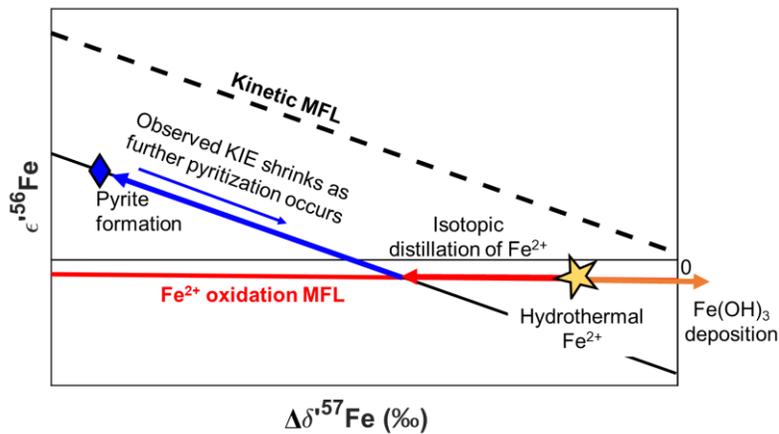
1120



1121
 1122 **Fig. S4.**
 1123 Rayleigh distillation effects in triple-Fe-isotopic space. A. Comparison of the effective MFL for
 1124 Rayleigh distillation (dotted line) with the instantaneous MFL for the fractionation between
 1125 reactant and product (solid line). The differing slopes result in a $\theta^{56/57}$ difference of just 0.0002,
 1126 well within achievable analytical error for natural ranges of fractionation. B. Comparison of the
 1127 effective mass fractionation array (dotted line) with the instantaneous MFL for the product
 1128 precipitation (solid line), for the case of pyrite precipitation from solution as a cumulative
 1129 Rayleigh distillation product with the maximum instantaneous fractionation $1000 \times (\alpha^{56}-1)$
 1130 of -3.1 ‰ suggested by ref. (14). The maximum deviation is less than 0.01 $\epsilon^{56}\text{Fe}$ units, well
 1131 within analytical error. Both reactant and product reservoir trends are identical to the
 1132 instantaneous MFL for the process driving Fe isotopic fractionation over the naturally observed
 1133 range of values within analytical error for $\epsilon^{56}\text{Fe}$ value, which is typically on the order of ± 0.05
 1134 (95 % C.I.).
 1135



1136



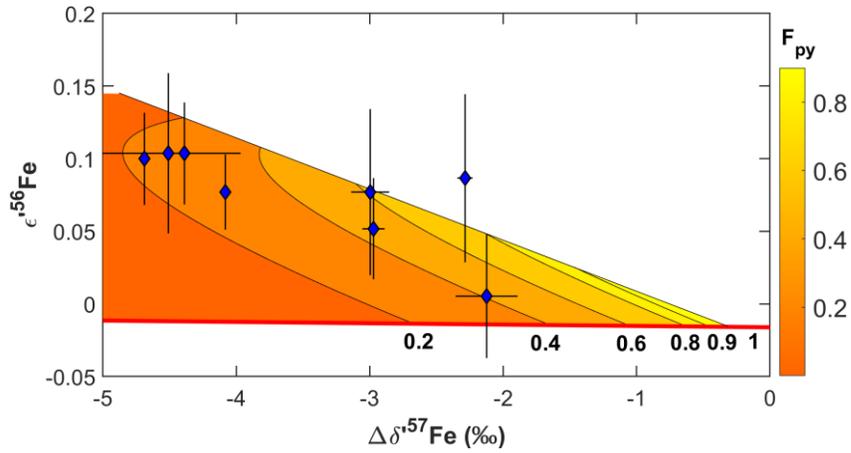
1137

1138 **Fig. S5.**

1139 Conceptual illustration of the two-step process (Fe^{2+} isotopic distillation by partial oxidation and
 1140 subsequent partial pyritization) that we propose for generating triple-Fe-isotopic composition of
 1141 isotopically depleted pre-GOE pyrites, and the procedure for determining Fe-isotopic contributions
 1142 of pyritization and initial isotopic composition of the pyrite-forming water mass to the Fe-isotopic
 1143 composition of pyrite. The $\Delta\delta^{57}\text{Fe}$ value at where a trajectory for KIE during pyrite precipitation
 1144 (with slope a_{KIE}) intercepts the oxidative IF MFL ($\Delta\delta^{57}\text{Fe}_w$) is determined by simultaneous solving
 1145 of two linear equations. The difference between $\Delta\delta^{57}\text{Fe}_w$ and $\Delta\delta^{57}\text{Fe}_{py}$ gives the expression of the
 1146 KIE during pyritization, which is used to determine the degree of pyritization (f_{py}) of the pre-
 1147 pyritization water mass, assuming that the pyrite is a cumulative product of all precipitated pyrite.
 1148 $\Delta\delta^{57}\text{Fe}_w$ is assumed to be the $\Delta\delta^{57}\text{Fe}$ value of the pre-pyritization water mass, and its isotopic
 1149 composition reflects the degree of isotopically heavy Fe^{3+} -oxyhydroxide removal (F_{ox}) that took
 1150 place prior to the formation of pyrite. $\Delta\delta^{57}\text{Fe}$ values are differences from IRMM-014.

1151

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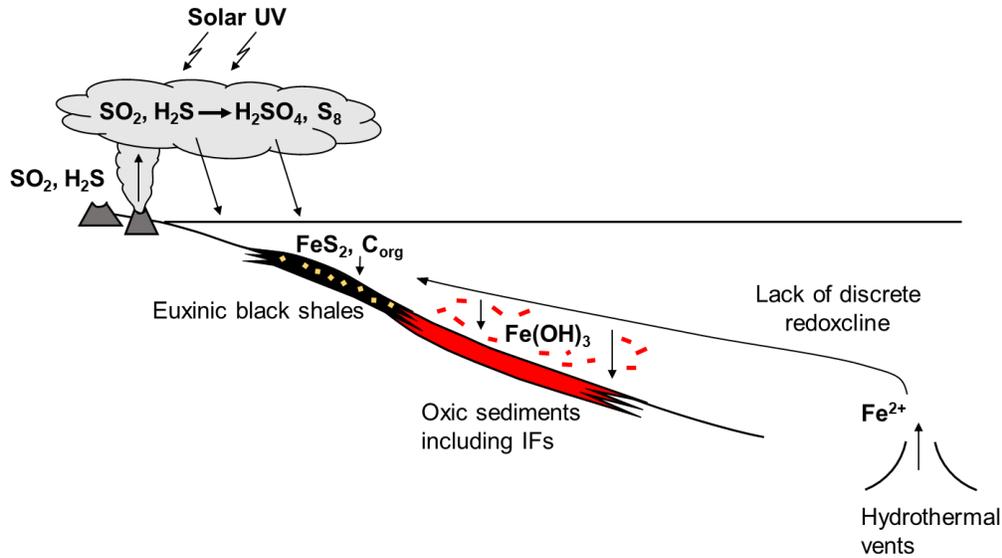


1153

1154 **Fig. S6.**

1155 Fractional pyrite sink for upwelled Fe (F_{py}) from triple-Fe-isotopic data. F_{py} values are calculated
 1156 as $F_{py} = f_{py} \times (1 - F_{ox})$. Corresponding f_{py} and F_{ox} contours are plotted in Figure 2C of the main
 1157 text. $\Delta\delta^{57}\text{Fe}$ values are differences from IRMM-014.

1158



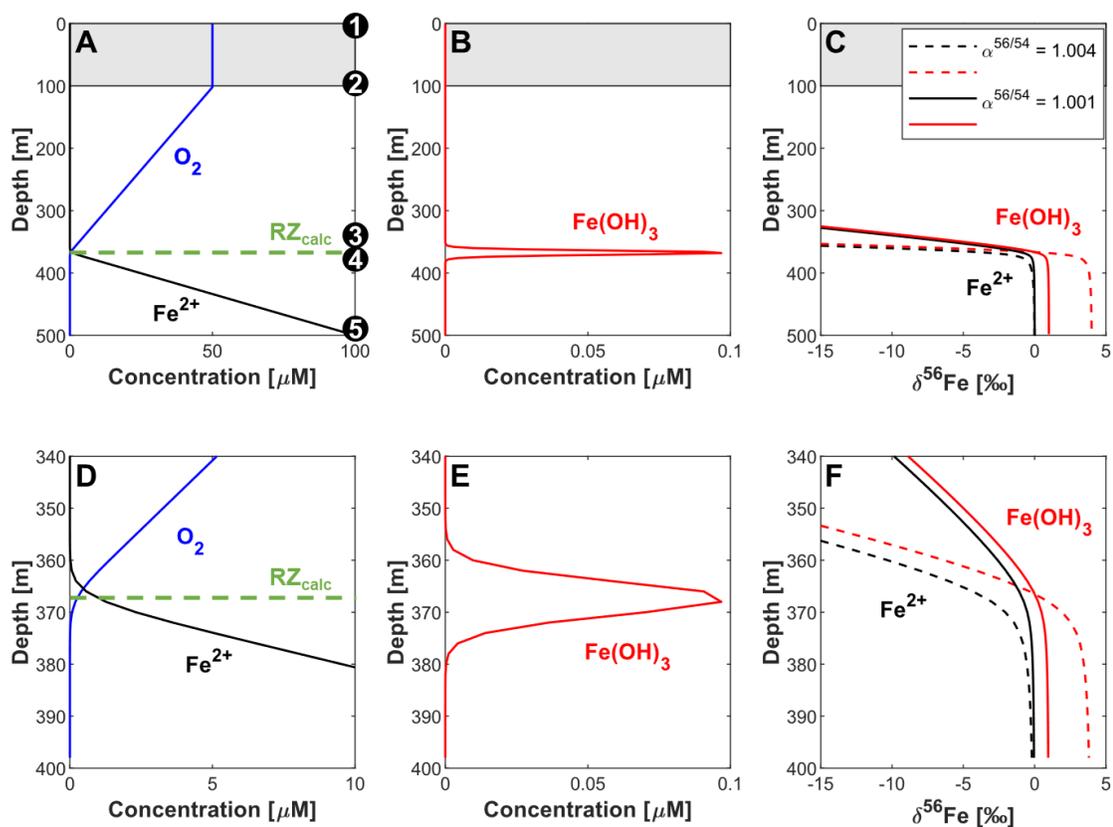
1159

1160 **Fig. S7.**

1161 Basin cross-section illustrating marine iron cycle before the GOE informed by triple-Fe-isotopic
 1162 systematics (9, 10, 31). Dissolved Fe^{2+} in deep-ocean waters fed by hydrothermal vents was
 1163 upwelled onto continental margins. Oxidation of Fe^{2+} across a spatially diffuse redoxcline led to
 1164 deposition of Fe^{3+} -oxyhydroxide-rich sediments including IFs. In sedimentary environments with
 1165 high organic carbon burial, the remaining dissolved Fe^{2+} was incorporated into pyrite, with
 1166 pyritization before the GOE being limited by sulfur availability controlled by volcanic outgassing.

1167

1168



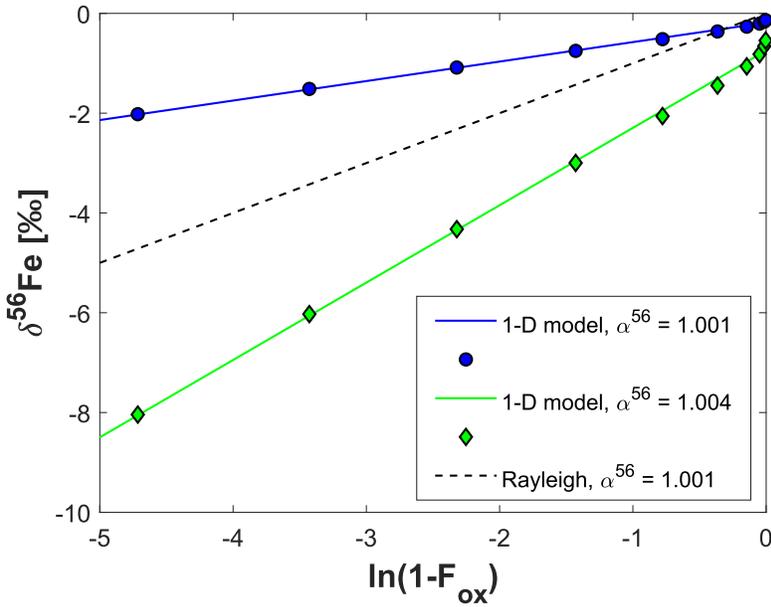
1169

1170 **Fig. S8**

1171 Depth profiles of outputs from 1-D dispersion-reaction model for Fe^{2+} oxidation (34). Input
 1172 parameters are given in Table S4. A. Depth profiles of O_2 (blue) and Fe^{2+} (black). The green dashed
 1173 line indicates the position of the reaction zone calculated using a simple scaling argument, and
 1174 agrees well with the depth in the model output where concentrations O_2 and Fe^{2+} go to zero as
 1175 $\text{Fe}(\text{OH})_3$ concentrations peak. Black circles indicate the layer numbers referred to in Equations
 1176 S14-S17. B. Depth profile of $\text{Fe}(\text{OH})_3$. C. Iron isotopic composition of Fe^{2+} (black) and $\text{Fe}(\text{OH})_3$
 1177 (red) using two different fractionation factors. D-F. As A-C, zoomed on the depth region
 1178 surrounding the reaction zone.

1179

1180

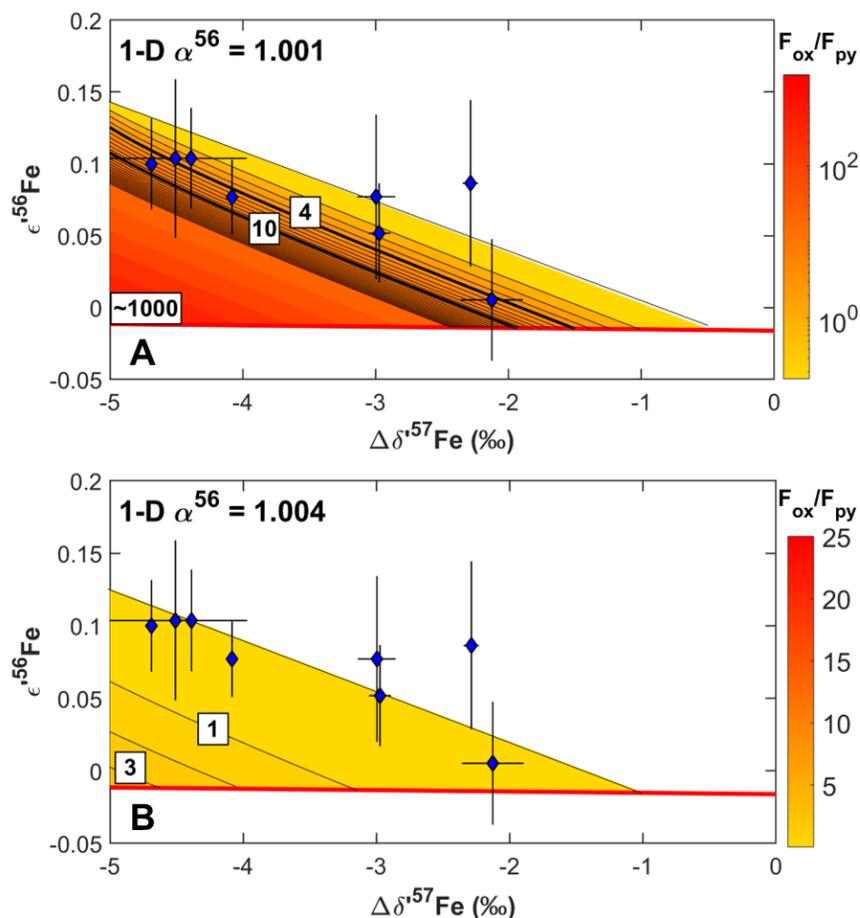


1181

1182 **Fig. S9**

1183 Evolution of the Fe isotopic composition of Fe^{2+} within the reaction zone of 1-D
 1184 dispersion-reaction models with different fractionation factors for $\text{Fe}(\text{OH})_3$ removal, as a function
 1185 of F_{ox} (calculated as the $\text{Fe}(\text{OH})_3$ formation rate integrated from the base of the model to variable
 1186 depths, normalized by the total integrated $\text{Fe}(\text{OH})_3$ precipitation in the model water column). All
 1187 arrays show linear relationships between $\delta^{56}\text{Fe}$ and $\ln(1-F_{\text{ox}})$, in the same manner as a Rayleigh
 1188 distillation model (dashed black line), but the slopes of these linear relationships are ~ 0.4 times
 1189 the slope expected for a Rayleigh distillation model with the same fractionation factor, α^{56} . Small
 1190 isotopic depletions at negligible values of F_{ox} likely reflect eddy diffusive effects.

1191



1192

1193 **Fig. S10**

1194 Pyrite triple-Fe-isotope data and contours of $F_{\text{ox}}/F_{\text{py}}$ (relative sizes of oxyhydroxide and pyrite
 1195 sedimentary Fe sinks) calculated using a 1-D dispersion-reaction model for isotopic fractionation
 1196 during Fe^{2+} oxidation (34). Bold contours at 4 and 10 indicate thresholds for net O_2 source vs. sink
 1197 behavior for volcanic $\text{H}_2\text{S}/\text{SO}_2$ inputs ratios of 1 (7) and 0 (8), respectively. A. Model using $\alpha^{56} =$
 1198 1.001 for Fe^{2+} oxidation. B. Model using $\alpha^{56} = 1.004$ for Fe^{2+} oxidation (following the approach
 1199 of ref. (34)). Contours in A are spaced in logarithmic scale. Pyrite triple-Fe-isotopic compositions
 1200 are consistent with net O_2 sources not being overwhelmed by Fe^{3+} oxyhydroxide formation.
 1201 $\Delta\delta^{57}\text{Fe}$ values are differences from IRMM-014.

1202

Table S1

Triple-Fe-isotope data for Archean-Paleoproterozoic (pre-GOE) pyrites, black shales, and IFs, normalized to exponential (exp) and high-T equilibrium limit (eq) laws

Sample	Age (Ga)	Sample type	$\delta^{156}\text{Fe}$	95% C.I.	$\delta^{157}\text{Fe}$	95% C.I.	$\epsilon^{156}\text{Fe}_{\text{exp}}$	$\epsilon^{156}\text{Fe}_{\text{eq}}$	95% C.I.	n
EBA-1 1057.5 Py	2.32	pyrite	1.034	0.153	1.527	0.229	0.080	-0.012	0.039	42
EBA 2/30 Py	2.32	pyrite	-2.023	0.095	-2.996	0.143	-0.103	0.077	0.057	12
DO29 14.95 Py	2.5	pyrite	-1.539	0.037	-2.286	0.057	-0.051	0.087	0.058	34
WB-98 520.8 Py	2.52	pyrite	-2.010	0.056	-2.972	0.083	-0.127	0.052	0.035	33
WB-98 519.68 Py	2.52	pyrite	-1.440	0.156	-2.125	0.232	-0.122	0.005	0.042	27
SF-1 599.88 Py	2.65	pyrite	-3.166	0.018	-4.688	0.025	-0.181	0.100	0.032	53
SF-1 623.6 Py	2.65	pyrite	-2.762	0.020	-4.082	0.028	-0.168	0.077	0.026	76
SF-1 642.8 Py	2.65	pyrite	-0.228	0.024	-0.343	0.035	0.029	0.049	0.039	55
FVG-1 752.8 A Py	2.66	pyrite	-3.046	0.367	-4.508	0.540	-0.167	0.104	0.055	21
FVG-1 752.8 B Py	2.66	pyrite	-2.967	0.020	-4.389	0.030	-0.160	0.104	0.035	55
EBA-1 1057.5 BS	2.32	black shale	0.072	0.091	0.105	0.139	-0.004	-0.011	0.042	46
FVG-1 765.8 BS	2.66	black shale	-0.546	0.064	-0.804	0.093	-0.051	0.065	0.059	12
FVG-1 774 BS	2.66	black shale	-1.577	0.123	-2.319	0.172	-0.074	0.008	0.051	29
FVG-1 827.8 BS	2.66	black shale	0.093	0.284	0.136	0.448	0.016	-0.003	0.201	10
REX 167.5	2.40	IF	-1.981	0.115	-2.915	0.168	-0.227	0.014	0.051	12
REX 187.5	2.40	IF	-2.692	0.008	-3.978	0.011	-0.224	-0.052	0.024	109
Hotazel #41	2.40	IF	-2.286	0.021	-3.354	0.032	-0.258	-0.056	0.046	39
RM5	2.47	IF	-0.008	0.276	-0.014	0.412	0.011	0.011	0.082	12
WIT-18-740A	2.48	IF	-1.199	0.067	-1.767	0.090	-0.111	-0.005	0.072	10
ZO4-31	2.70	IF	0.796	0.132	1.169	0.200	0.085	0.015	0.059	26
JD-C165A	2.74	IF	1.624	0.019	2.407	0.028	0.126	-0.019	0.019	184
JD-65-296-1	2.74	IF	1.030	0.265	1.527	0.396	0.002	-0.090	0.052	23
PO5-1	2.95	IF	-1.384	0.028	-2.039	0.039	-0.103	-0.016	0.031	55
PO5-6	2.95	IF	-0.696	0.142	-1.028	0.210	-0.065	0.019	0.074	26
PO5-7	2.95	IF	-1.290	0.224	-1.900	0.336	-0.130	-0.004	0.037	12
IF-G	3.83	IF	0.611	0.012	0.878	0.019	0.052	-0.001	0.030	24

All isotope ratios are reported normalized to IRMM-524, which has an isotopic composition identical to IRMM-014 (43). The value of n refers to the total number of standard-sample brackets analyzed. $\delta^{157}\text{Fe}$ and $\epsilon^{156}\text{Fe}$ were determined from the same analyses. δ' values for natural samples are discussed as $\Delta\delta'$ values (differences from IRMM-014) in the text.

Triple-Fe-isotopic data for pyrite precipitation experiments, normalized to exponential (exp) and high-T equilibrium limit (eq) laws													
Sample	$\delta^{56}\text{Fe}$	$\delta^{56}\text{Fe}-\delta^{56}\text{Fe}_0$	95% C.I.	$\delta^{57}\text{Fe}$	$\delta^{57}\text{Fe}-\delta^{57}\text{Fe}_0$	95% C.I.	n(δ')	$\epsilon^{56}\text{Fe}_{\text{exp}}$, IRMM-524	$\epsilon^{56}\text{Fe}_{\text{eq}}$, IRMM-524	$\epsilon^{56}\text{Fe}_{\text{exp}}$	$\epsilon^{56}\text{Fe}_{\text{eq}}$	95% C.I.	n(ϵ')
SB1-4 initial	0.262		0.045	0.371		0.064	5	0.031	0.009			0.020	40
SB5-10 initial	0.236		0.041	0.414		0.081	5	0.027	0.002			0.014	76
SB1 FeS	0.505	0.243	0.045	0.752	0.381	0.064	5	0.080	0.035	0.049	0.027	0.039	21
SB1 Py	-1.939	-2.201	0.045	-2.897	-3.269	0.064	5	-0.039	0.134	-0.070	0.126	0.040	26
SB2 FeS	0.421	0.159	0.045	0.647	0.276	0.064	5	0.028	-0.011	-0.003	-0.020	0.074	10
SB2 Py	-2.320	-2.582	0.045	-3.168	-3.540	0.064	5	-0.061	0.129	-0.092	0.120	0.054	9
SB3 FeS	0.494	0.232	0.045	0.697	0.326	0.064	5	0.040	-0.002	0.009	-0.010	0.053	20
SB3 Py	-1.810	-2.072	0.045	-2.708	-3.080	0.064	5	-0.069	0.093	-0.100	0.084	0.031	17
SB4 FeS	0.564	0.302	0.045	0.818	0.447	0.064	5	0.024	-0.025	-0.007	-0.034	0.049	9
SB4 Py	-1.816	-2.078	0.045	-2.705	-3.077	0.064	5	-0.061	0.101	-0.092	0.092	0.055	10
SB5 FeS	0.353	0.117	0.041	0.547	0.133	0.081	5	0.028	-0.005	0.001	-0.007	0.069	9
SB5 Py	-1.915	-2.151	0.041	-2.885	-3.300	0.081	5	-0.019	0.153	-0.046	0.152	0.021	27
SB6 FeS	0.412	0.176	0.041	0.587	0.173	0.081	5	0.030	-0.005	0.003	-0.007	0.055	9
SB6 Py	-1.777	-2.013	0.041	-2.668	-3.083	0.081	5	-0.049	0.111	-0.076	0.109	0.046	9
SB8 FeS	0.551	0.315	0.041	0.775	0.361	0.081	5	0.046	-0.001	0.019	-0.003	0.043	20
SB8 Py	-1.755	-1.991	0.041	-2.600	-3.016	0.081	5	0.001	0.157	-0.026	0.155	0.023	28
SB9 FeS	0.563	0.327	0.041	0.845	0.431	0.081	5	0.069	0.018	0.042	0.016	0.031	27
SB9 Py	-1.636	-1.873	0.041	-2.415	-2.830	0.081	5	-0.037	0.108	-0.063	0.106	0.060	20
SB10 FeS	0.620	0.384	0.041	0.919	0.505	0.081	5	0.035	-0.020	0.008	-0.022	0.036	29
SB10 Py	-1.693	-1.930	0.041	-2.491	-2.906	0.081	5	-0.062	0.088	-0.088	0.086	0.035	28

δ' and $\epsilon^{56}\text{Fe}_{\text{IRMM-524}}$ values are reported normalized to IRMM-524, which has an isotopic composition identical to IRMM-014 (43). $\delta'-\delta'_0$ values are the differences between FeS and pyrite samples and the starting material for the experiments and are equivalent to the $\Delta\delta'$ values discussed in the text. $\epsilon^{56}\text{Fe}$ is defined in the text based on differences from the starting material, so $\epsilon^{56}\text{Fe}$ values given here and displayed in the figures reflect differences between the $\epsilon^{56}\text{Fe}_{\text{IRMM-524}}$ values of the experimental products (FeS: residual FeS, and Py: pyrite precipitate) and the $\epsilon^{56}\text{Fe}_{\text{IRMM-524}}$ values of the respective initial batches of starting FeS (used for samples SB1-4, and SB5-10). The values of n(δ') and n(ϵ') refer to the total number of standard-sample brackets analyzed for δ' and ϵ' measurements, respectively. δ' and ϵ' measurements were made separately using different analytical methods, detailed in the text. Starting material for samples SB1-4 and SB5-10 were analyzed 40 and 76 times, respectively.

Table S3				
Geological unit and age information for Archean-Paleoproterozoic pyrite, black shales, and IFs				
Sample	Geological unit	Age (Ga)	Sample type	Refs.
EBA-1 1057.5 Py	Timeball Hill Fm	2.32	pyrite	(9)
EBA 2/30 Py	Timeball Hill Fm	2.32	pyrite	(9)
DO29 14.95 Py	Mount McRae Shale	2.50	pyrite	(9)
WB-98 520.8 Py	Gamohaam Fm	2.52	pyrite	(9)
WB-98 519.68 Py	Gamohaam Fm	2.52	pyrite	(9)
SF-1 599.88 Py	Lokammona Fm	2.65	pyrite	(9)
SF-1 623.6 Py	Lokammona Fm	2.65	pyrite	(9)
SF-1 642.8 Py	Lokammona Fm	2.65	pyrite	(9)
FVG-1 752.8 A Py	Jeerinah Fm	2.66	pyrite	(9)
FVG-1 752.8 B Py	Jeerinah Fm	2.66	pyrite	(9)
EBA-1 1057.5 BS	Timeball Hill Fm	2.32	black shale	(9, 30)
FVG-1 765.8 BS	Jeerinah Fm	2.66	black shale	(9, 30)
FVG-1 774 BS	Jeerinah Fm	2.66	black shale	(9, 30)
FVG-1 827.8 BS	Jeerinah Fm	2.66	black shale	(9, 30)
REX 167.5	Hotazel Fm	2.43	IF	(2, 28, 55)
REX 187.5	Hotazel Fm	2.43	IF	(2, 28, 55)
Hotazel #41	Hotazel Fm	2.43	IF	(2, 28, 55)
RM5	Brockman IF	2.47	IF	(10)
WIT-18-740A	Westerburg area IF	2.48	IF	(10)
ZO4-31	Manjeri IF	2.70	IF	(10)
JD-C165A	Mary River IF	2.74	IF	(10)
JD-65-296-1	Mary River IF	2.74	IF	(10)
PO5-1	Mozaan Gp	2.95	IF	(10)
PO5-6	Mozaan Gp	2.95	IF	(10)
PO5-7	Mozaan Gp	2.95	IF	(10)
IF-G	Isua Supracrustal Belt	3.83	IF	(54, 56)

Reference numbers refer to Supplementary Reference List in the Supplementary Information

Table S4		
Fe-O ₂ dispersion-reaction steady-state model parameters		
Parameter		Value
Water column depth (m)		500
Eddy diffusion coefficient (cm² s⁻¹)		0.1
[O₂] (μmol L⁻¹)	Upper (within photic zone)	50
	Lower	No-flux
[Fe²⁺] (μmol L⁻¹)	Upper	No-flux
	Lower	100
Photic zone depth range (m)		0-100
Temperature (°C)		25
Salinity (ppt)		35
Fe(OH)₃ settling rate constant (day⁻¹)		0.79
Simulation time (yrs)		2000
δ⁵⁶Fe_{Fe2+,initial} (‰)		0
α_{Fe(OH)3-Fe2+}		1.001, 1.002, 1.004
Input parameters match those of Czaja <i>et al.</i> (2012) (34), except the fixed photic-zone [O ₂], which matches the value reached at the base of the photic zone in Czaja <i>et al.</i> (34), for the equivalent model run (run 1 in that study).		

Table S5						
Estimated fractional size of iron sinks and shelf sedimentary Fe/S ratios for isotopically light pyrites						
Sample	Age bin (Ga)	F_{ox}	f_{py}	F_{py}	Moles O₂ yield (per mole FeS₂)	Age-bin average O₂ yield
EBA 2/30	2.32	0.47 ^{+0.45} _{-0.42}	0.69 ^{+0.31} _{-0.51}	0.43 ^{+0.18} _{-0.32}	0.35 (1.06)	0.35 (1.06)
DO29 14.95	2.50-2.52	0.33 ^{+0.56} _{-0.25}	0.57 ^{+0.41} _{-0.51}	0.58 ^{+0.19} _{-0.35}	0.55 (1.51)	0.30 ± 0.21 (0.96 ± 0.47)
WB-98 520.8	2.50-2.52	0.59 ^{+0.18} _{-0.54}	0.84 ^{+0.16} _{-0.51}	0.36 ^{+0.26} _{-0.26}	0.23 (0.80)	0.30 ± 0.21 (0.966 ± 0.47)
WB-98 519.68	2.50-2.52	0.71 ^{+0.19} _{-0.59}	0.99 ^{+0.01} _{-0.27}	0.29 ^{+0.44} _{-0.23}	0.12 (0.56)	0.30 ± 0.21 (0.96 ± 0.47)
SF-1 599.88	2.65-2.66	0.70 ^{+0.23} _{-0.60}	0.65 ^{+0.35} _{-0.58}	0.18 ^{+0.04} _{-0.13}	0.003 (0.31)	0.05 ± 0.02 (0.41 ± 0.05)
SF-1 623.6	2.65-2.66	0.70 ^{+0.24} _{-0.60}	0.75 ^{+0.25} _{-0.59}	0.23 ^{+0.10} _{-0.17}	0.06 (0.42)	0.05 ± 0.02 (0.41 ± 0.05)
FVG-1 752.8 A	2.65-2.66	0.67 ^{+0.28} _{-0.59}	0.63 ^{+0.37} _{-0.58}	0.21 ^{+0.04} _{-0.16}	0.04 (0.39)	0.05 ± 0.02 (0.41 ± 0.05)
FVG-1 752.8 B	2.65-2.66	0.62 ^{+0.31} _{-0.55}	0.58 ^{+0.40} _{-0.52}	0.24 ^{+0.03} _{-0.17}	0.10 (0.51)	0.05 ± 0.02 (0.41 ± 0.05)

For F_{ox}, f_{py}, and F_{py} values, central estimates are 50% percentiles, and uncertainties are 95 % C.I. from Monte Carlo simulations. For O₂ yields, central estimates are calculated from central estimates for F_{ox} and F_{py} values. The first number assumes volcanic H₂S/SO₂ input ratio of 1 (7), second number (in parentheses) assumes volcanic H₂S/SO₂ input ratio of 0 (8). Error bars for Age-bin averages are the 95 % C.I. of the average values.