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4 **Resolving the Role of Ocean Iron Sinks in Early**
5 **Atmospheric Oxygenation**
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33 **Abstract (113 words)**

34 The role that iron played in the oxygenation of Earth's surface is equivocal. Iron could have
35 consumed O₂ during Fe²⁺ oxidation or released O₂ during pyrite burial fueled by volcanic
36 SO₂. Through high-precision Fe isotopic measurements of Archean-Paleoproterozoic sediments
37 and laboratory grown pyrites, we show that the triple-Fe-isotopic composition of Neoproterozoic-
38 Paleoproterozoic pyrites requires both extensive marine iron oxidation and sulfide-limited
39 pyritization. Using an isotopic fractionation model informed by these new constraints, we resolve
40 the relative sizes of marine oxide and pyrite sinks for Neoproterozoic marine iron. We show that pyrite
41 burial could have resulted in O₂ export exceeding local Fe²⁺ oxidation sinks, thus contributing to
42 early episodes of oxygenation of the Archean atmosphere.

43 **Main Text**

44 Irreversible changes of oxic and euxinic sedimentary iron sinks during the Archean and
45 Paleoproterozoic were intimately linked with the oxygenation of Earth's atmosphere during the
46 Great Oxygenation Event (GOE), beginning ca. 2.43 Ga (1, 2). Early episodes of oxygenation
47 coincided with enhanced burial of iron sulfide (pyrite) in sediments (3–5). This limb of the pre-
48 GOE Fe cycle may have directly contributed to early atmospheric oxygenation, as enhanced
49 volcanic SO₂ fluxes accompanying Neoproterozoic continental emergence may have contributed to
50 net burial of reducing power in sedimentary pyrite, following microbial sulfate reduction (6–8).
51 Early environmental oxidation should have been buffered by reduced species in the ocean and
52 atmosphere, principally Fe²⁺. Therefore, the marine iron cycle potentially played roles on both
53 sides of Earth's early oxygenation. Major shifts in Fe isotopic records occur across the GOE (9,
54 10) (Fig. 1A), and reflect evolution of the Fe, S, and O cycles through the Archean and
55 Paleoproterozoic (11). Interpretation of the Fe isotopic composition of pre-GOE pyrites, which
56 can be depleted in ⁵⁶Fe/⁵⁴Fe ratio by as much as -3.5‰, a degree unseen in the post-GOE rock
57 record (9), is however not straightforward. The reason is that these pyrite Fe isotopic compositions
58 could be controlled by (i) the size of oxidizing iron sinks that removed isotopically heavy Fe³⁺
59 oxides, leaving a pool of isotopically light dissolved Fe²⁺ from which pyrite could have formed (9,
60 10); (ii) microbial dissimilatory Fe³⁺ reduction (DIR) that preferentially releases an isotopically
61 light Fe²⁺ pool (12, 13); and (iii) kinetic isotope effects (KIEs) accompanying partial pyrite
62 precipitation, which can produce isotopically light pyrite (14, 15). The relative importance of these
63 processes remains heavily debated (9–18), and this uncertainty has hindered quantitative
64 interpretation of the ancient iron cycle, exemplified by the fact that δ⁵⁶Fe records have not yet
65 constrained the degree to which Fe sedimentation on highly productive continental margins was a
66 net sink or source for early O₂ (8).

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

74 in magmatic olivine followed a kinetic MFL for diffusive transport (21). For a given MFL, the
75 ratio of $^{56}\text{Fe}/^{54}\text{Fe}$ to that of $^{57}\text{Fe}/^{54}\text{Fe}$ defines the slope

$$76 \quad \theta^{56/57} = \delta^{56}\text{Fe}/\delta^{57}\text{Fe} \quad (\text{Eq. 1})$$

77 where $\delta^x\text{Fe} = 1,000 \ln[(^x\text{Fe}/^{54}\text{Fe})_{\text{sample}}/(^x\text{Fe}/^{54}\text{Fe})_{\text{IRMM-014}}]$ (IRMM-014 is a standard reference
78 material consistent with bulk planetary composition) (20, 22). Isotopic trends following an array
79 of MFLs are by definition mass-dependent; but they manifest as apparent departures, $\epsilon^{56}\text{Fe}$, from
80 an arbitrary reference MFL (20, 23, 24), which we choose here to be the high-temperature
81 equilibrium limit law with $\theta^{56/57}=0.678$, where

$$82 \quad \epsilon^{56}\text{Fe} = [\delta^{56}\text{Fe} - 0.678 \times \delta^{57}\text{Fe}] \times 10 \quad (\text{Eq. 2})$$

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

$$85 \quad \epsilon^{56}\text{Fe} = 10 \times [\theta^{56/57} - 0.678] \times \delta^{57}\text{Fe} \quad (\text{Eq. 3})$$

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

88 (i) A suite of iron formation (IF) samples that show a large range in $\delta^{56}\text{Fe}$ values, including
89 Mn-rich IFs from the Hotazel Formation in the Griqualand West sub-basin, South Africa, dated at
90 ca. 2.43 Ga (2), that were presumably precipitated from an iron pool that had experienced extensive
91 oxidative iron removal, resulting in IFs characterized by anomalously low $\delta^{56}\text{Fe}$ values (25).

92 (ii) Experimental products of pyrite synthesis via the FeS-H₂S pathway, which produced
93 pyrite with $\delta^{56}\text{Fe}$ values as low as -2.4‰ relative to the initial iron pool (Figs. 1B, S2) (24). In
94 these experiments, we precipitated pyrite in anoxic conditions from an FeS precursor (24)
95 following a protocol established by Guilbaud et al. (14, 24).

96 The IFs define a slope of $\theta^{56/57}_{\text{ox}}=0.6776\pm 0.0004$ for the oxidizing (_{ox}) iron sink (here and
97 elsewhere, the error bars are 95% confidence intervals), which agrees with theoretical expectations
98 for equilibrium isotope exchange that dominates during iron oxidation (20, 22), while the pyrite-
99 precipitation experiments gave $\theta^{56/57}_{\text{KIE}}=0.6743\pm 0.0006$ (Fig. 1B). Triple-Fe-isotopic slopes for
100 the two endmember scenarios are clearly distinct, allowing us to use these slopes to address what
101 caused Fe isotopic variations in natural pyrites before the GOE.

102 We analyzed a suite of pre-GOE Neoproterozoic-Paleoproterozoic pyrites with highly depleted
103 $\delta^{56}\text{Fe}$ values (as low as -3.1 ‰) and a few bulk black shales from the same formations. The pyrite
104 and shales fall in an intermediate space in the triple Fe isotope diagram between the endmember

105 MFLs for Fe²⁺ oxidation and pyrite precipitation. A linear regression through these data would
106 have a slope of 0.6761±0.0006, but we do not interpret the apparent linear trend as an MFL,
107 because the pyrite and shale array is composed of samples from several distinct formation and
108 each sample requires contributions from more than one fractionation process (with distinct MFLs)
109 and therefore has no mechanistic significance. More likely, pre-GOE pyrite δ⁵⁶Fe values record a
110 two-step process; partial marine Fe²⁺ oxidation during non-steady-state upwelling of Fe²⁺-rich
111 deep waters (9), and subsequent KIEs during partial, sulfide-limited pyrite formation from the
112 remaining Fe²⁺ reservoir (14, 15, 26). In this model, oxic and pyrite sinks sequestered iron
113 upwelling from deep ocean basins lacking a discrete redoxcline, towards black shale depositional
114 settings (Fig. S7)(10, 24, 27) .

115 For any isotopically light pyrite sample, we can estimate contributions to the δ⁵⁶Fe value from
116 prior iron-oxidation, and the KIE during pyritization in the porewater iron reservoir. We calculate
117 contributions of Fe-oxidation to δ⁵⁶Fe values of the water mass (δ⁵⁶Fe_w) from intercepts with the
118 oxidation MFL, and determined the Fe isotopic fractionation imparted by pyritization by taking
119 the difference in δ⁵⁶Fe values between those of pyrite and δ⁵⁶Fe_w (Figs. 2A, S5) (24). An
120 underlying assumption in this calculation is that sedimentary pyrite formed from a pool of
121 dissolved Fe²⁺ that sampled the marine Fe²⁺ reservoir (9), although the nodular nature of the pyrites
122 indicates that they formed in sediments through diagenesis. A major source of iron in porewaters
123 would presumably have been downward diffusion of overlying Fe²⁺-rich seawater into the
124 sediment (9). We cannot exclude however that some porewater Fe²⁺ was produced by DIR (12,
125 13). This is an uncertainty in our model. However, the role of partial (isotopically fractionating)
126 DIR in the host shales of these pyrites is not supported by Fe isotopic compositions of bulk shale
127 material, which lacks the complimentary heavy isotopic signature that would be expected of a DIR
128 residue (26). Additionally, coupled Fe and C isotope analyses of Archean sediments suggests that
129 DIR occurred in a closed system with respect to isotopes, with diagenetic carbonate minerals
130 taking on the composition of their precursor oxides (28, 29). While we cannot rule out the
131 additional influence of DIR in the origin of pre-GOE pyrite Fe isotopic signatures, we anticipate
132 that any uncertainty it introduces would be transferred to interpretations of δ⁵⁶Fe_w values, and not
133 the departures of triple Fe isotopic values from the Fe²⁺ oxidation MFL. The reason for this is that
134 experiments to date suggest that the isotopic fractionation during DIR is an expression of the

135 equilibration of Fe^{2+} and Fe^{3+} after the reduction step (30), and therefore we expect it would fall
136 into the same class of Fe redox equilibrium processes that define the Fe^{2+} oxidation MFL.

137 The fraction of Fe^{3+} -(oxyhydr)oxide removed to give the $\delta^{56}\text{Fe}_w$ value on the intercept
138 ($F_{\text{ox}} = \text{Fe in oxide sink/total Fe}$), and the fraction of pyrite removed from that remaining Fe^{2+} pool
139 ($f_{\text{py}} = \text{Fe in pyrite/Fe remaining after Fe removal in the oxide sink}$), are both calculated assuming
140 Rayleigh fractionation conditions (Figs. 2, S5; Table S4) (24) following upwelling of Fe^{2+} -rich
141 deep water across the redoxcline (Fig. 2B). The fractional pyrite sink F_{py} for iron in the whole
142 depositional system is $F_{\text{py}} = f_{\text{py}} \times (1 - F_{\text{ox}})$. Values of F_{ox} increase heading to more negative $\delta^{57}\text{Fe}$
143 and $\epsilon^{56}\text{Fe}$ values, whereas f_{py} decrease away from the oxidation MFL, reflecting preservation of a
144 larger KIE at lower degrees of pyritization (Fig. 2B). F_{py} decreases strongly with decreasing $\delta^{57}\text{Fe}$,
145 due to the combined effects of decreasing f_{py} and increasing F_{ox} in this direction (Fig.S5). Contours
146 of $F_{\text{ox}}/F_{\text{py}}$ are sub-horizontal, making $\epsilon^{56}\text{Fe}$ measurements highly diagnostic of the relative size of
147 the oxic and pyritic sinks (Fig. 2C).

148 To fully propagate the effect of uncertainties in sample measurements; $\theta^{56/57}$ values for the
149 endmember processes; and model fractionation factors; on uncertainties in F_{ox} , f_{py} , and F_{py} , we
150 also used a Monte-Carlo simulation (Fig. 3). Estimates for F_{py} are 10 – 80 % of the upwelled iron
151 pool (within 95 % C.I.) among the low $\delta^{56}\text{Fe}$ pyrites we studied. With initial pre-GOE deep-water
152 $[\text{Fe}^{2+}]$ concentrations $\sim 50 \mu\text{M}$ (1), the pyrite sink could have removed 5-40 μM of dissolved iron.
153 This requires ~ 10 -80 μM of seawater-dissolved sulfate to be microbially reduced to sulfide, ~ 350
154 to 1,400 times lower than the modern seawater sulfate concentration of 28 mM, and within recent
155 estimates for Archean seawater sulfate based on S isotopic modelling (31, 32). For the ~ 2.65 Ga
156 Jeerinah and Lokammona formations, we infer that as little as 10 % of iron upwelled onto the shelf
157 was deposited as pyrite in euxinic sediments (Figs 2B, 3, S6) (24).

158 When volcanic SO_2 is the primary sulfur source, burial of reduced S in pyrite has a net
159 oxidative effect on Earth's surface (6–8). For example, the reaction $2\text{SO}_2 + \text{H}_2\text{O} + \text{Fe}^{2+} \rightarrow \text{FeS}_2 +$
160 $2\text{H}^+ + 2.5\text{O}_2$, describing the net effect of SO_2 photolysis and hydrolysis, cyanobacterial
161 photosynthesis, microbial sulfate reduction, and pyrite precipitation, indicates that pyrite burial
162 can directly promote the net export of O_2 to the atmosphere-ocean system (8). The reaction is a
163 maximum estimate for O_2 export during pyrite burial, because a more reduced original sulfur
164 source would weaken the net oxidative effect of pyrite burial; and other types of primary
165 productivity could have contributed organic matter for sulfate reduction, but only cyanobacterial

166 activity could have produced O₂. A more realistic estimate of volcanic H₂S/SO₂ emission ratios ~1
167 (7) would instead imply a net O₂ yield of 1 mole per mole of pyrite buried.

168 To oxygenate the atmosphere via pyrite burial, the produced O₂ would also need to overcome
169 O₂ buffers in the ocean, primarily the upwelled Fe²⁺ flux. O₂-driven Fe²⁺ oxidation consumes 0.25
170 moles of O₂ per mole of Fe³⁺ buried, so net O₂ sources and sinks will be balance when
171 F_{ox}/F_{py} = 4 (10) for volcanic H₂S/SO₂ emission ratios = 1 (0). Lower (higher) F_{ox}/F_{py} ratios
172 indicate that Fe sedimentation in these settings was a net source (sink) of O₂ to the ocean-
173 atmosphere system. Triple-Fe-isotopic systematics are strongly diagnostic for F_{ox}/F_{py} ratios,
174 particularly at high values of this ratio where the switch from net O₂ source to sink behavior occurs
175 (Fig. 2C). Pre-GOE pyrite data all fall at F_{ox}/F_{py} < 4 contour, and the F_{ox}/F_{py} < 10 falls outside of
176 the error bar on individual pyrite ε⁵⁶Fe values, so we can robustly rule out net O₂ sink-like behavior
177 in the case where SO₂ dominated Neoproterozoic volcanic emissions. Even with conservative H₂S/SO₂
178 ratios (7) our data would imply a net O₂ source existed in Neoproterozoic pyrite-forming
179 environments, particularly after 2.52 Ga (Figs 2C, 3). Average results from Monte Carlo
180 simulations imply that the majority (>70 %) of O₂ liberated during pyrite burial could have
181 remained to be released to the ocean-atmosphere system after exhausting local Fe²⁺ oxidation
182 sinks. Despite the large net O₂ yield implied by all the formations we studied, evidence for whiffs
183 of O₂ at ca. 2.65 Ga is weak (33) compared to the ca. 2.5 Ga event recorded by the Mt McRae
184 Shale (4, 34). The ca. 2.65 Ga Jeerinah and Lokammona formations indicate higher relative F_{ox}/F_{py}
185 ratios and lower net O₂ yields (Figs 2C, 3). This raises the possibility that the real (non-idealized)
186 threshold value for net O₂ release during Fe upwelling and pyrite burial lies on a F_{ox}/F_{py} contour
187 separating 2.65 Ga pyrites (represented by the four most isotopically depleted pyrite samples in
188 this study) from younger, higher δ⁵⁶Fe samples (Fig. 2C).

189 The triple-Fe-isotope proxy provides a new and greater insight to the iron cycle in the early
190 Earth's oceans. Before the GOE, large and probably fluctuating continental and hydrothermal iron
191 fluxes to the oceans (27) were removed to two sedimentary sinks (Fig. S7)(24). The major sink
192 was Fe³⁺-(oxyhydr)oxides that were deposited from upwelling water masses in the oceans that
193 lacked a discrete redoxcline and allowed protracted partial iron oxidation (9, 10). The secondary
194 iron sink was on highly productive continental margins, where deposition of pyrite-rich sediments
195 was generally sulfate-limited. Small relative changes in iron removal to these oxide and sulfide
196 sinks potentially led to perturbations in the net O₂ supply to the atmosphere, and surface ocean

197 oxygenation (6, 7), triggering short-lived, episodic whiffs of O₂ (8). The loss of extremely negative
198 $\delta^{56}\text{Fe}$ values in sedimentary pyrite formed after the GOE shows how this transition irreversibly
199 changed the early Earth's iron cycle by decreasing iron flux to the oceans following the emergence
200 of oxidative continental weathering; developing a discrete water-column redoxcline; and
201 increasing supply of sulfate from the continents, which resulted in a shift in the major iron sink to
202 extensively developed euxinic settings.

203

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355 **List of Supplementary Materials:**

356 Materials and Methods

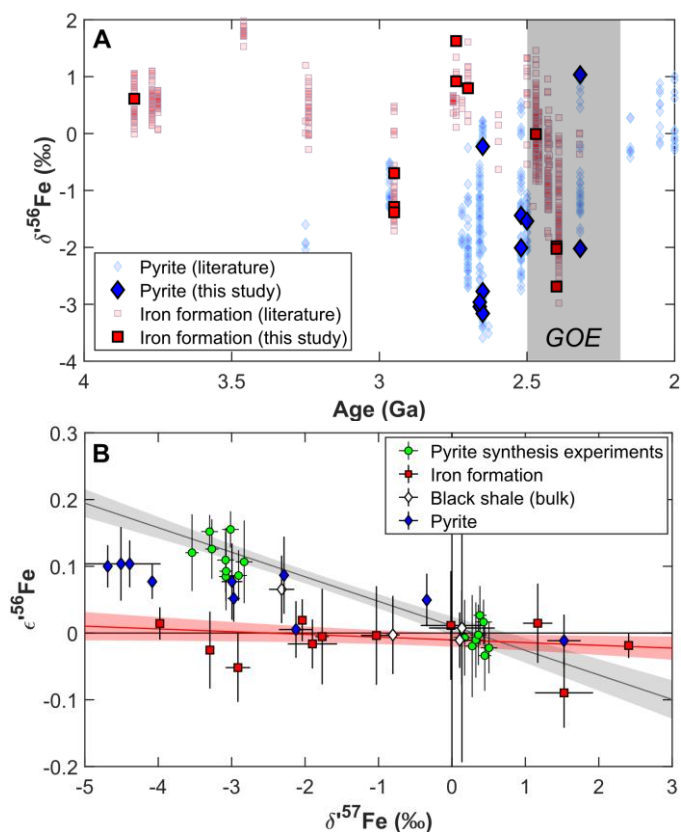
357 Supplementary Text

358 Figs. S1 to S7

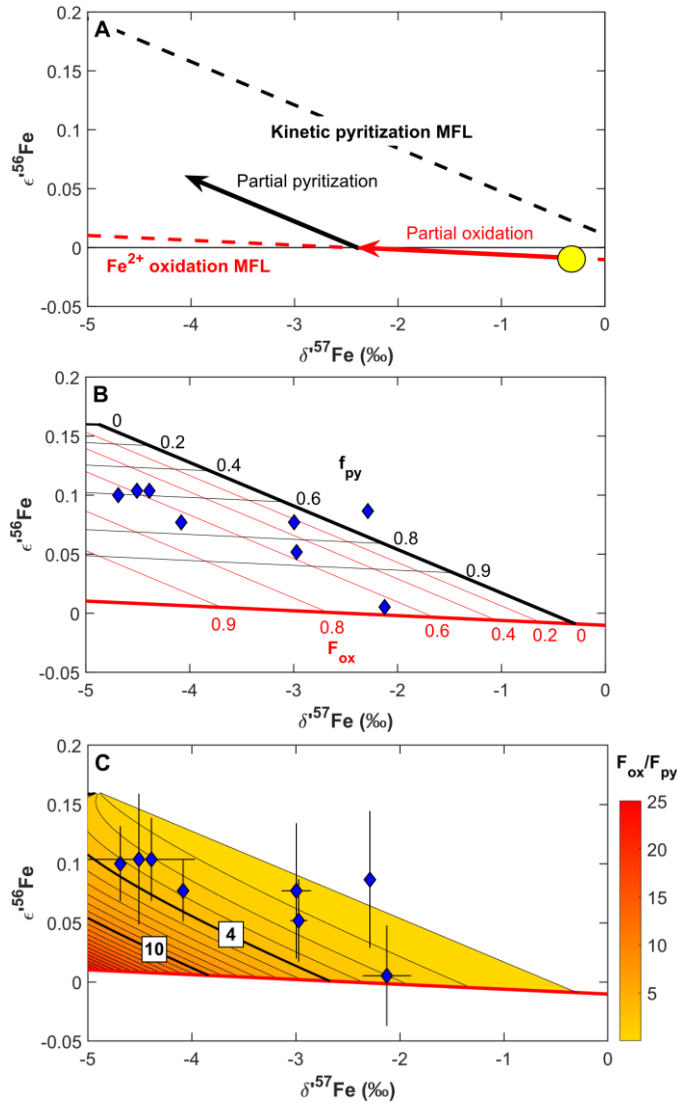
359 Tables S1 to S4

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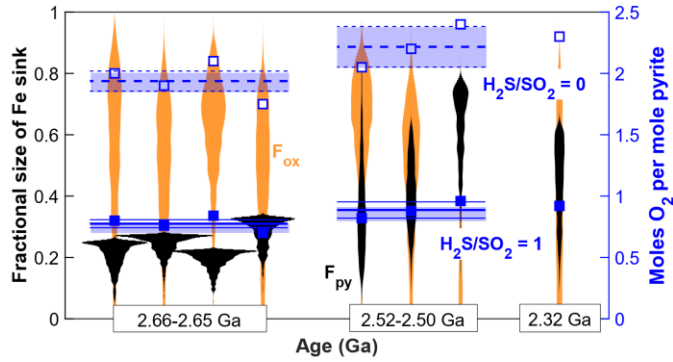
363 **Fig. 1.**

364 Iron isotope systematics of pre-GOE sediments and pyrites, and pyrites produced in laboratory
 365 experiments. A) $\delta^{56}\text{Fe}$ values of IFs and pyrites analyzed in this study, plotted against their ages
 366 on the horizontal axis, relative to published IF and pyrite data. B) Triple-Fe-isotope systematics
 367 for IFs, pyrites, and black shales in $\epsilon^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$ space. Error bars and envelopes are 95%
 368 confidence intervals. The slopes of endmember MFLs associated with iron-redox processes, and
 369 KIEs during pyritization, are constrained through analysis of isotopically light Mn-rich IFs and
 370 laboratory pyrite precipitation via the H_2S pathway (14, 24, 35), respectively. The slope of the IF
 371 MFL agrees with the theoretical equilibrium law (defined by the horizontal axis at $\epsilon^{56}\text{Fe} = 0$),
 372 implying control by Fe^{2+} - Fe^{3+} equilibrium (20, 22). Pyrite synthesis defines a kinetic MFL for
 373 pyrite precipitation. Pre-GOE pyrites fall in an intermediate space between redox equilibrium and
 374 kinetic endmembers.



376 **Fig. 2.**

377 Interpreting triple-Fe-isotopic signatures of isotopically light pyrites. A) Schematic of two-step
 378 process involved in pyrite formation. Iron with starting compositions resembling hydrothermal
 379 fluids (gold circle) is oxidized, driving residual Fe²⁺ to light compositions along the Fe²⁺ oxidation
 380 MFL. Partial pyrite precipitation from this Fe²⁺ subsequently causes fractionations along the
 381 kinetic pyrite formation MFL. The approach is detailed in Figure S4 and equations in (24). B)
 382 Pyrite data and contours for F_{ox} and f_{py} in triple Fe isotope space. F_{py} , the fraction of total upwelled
 383 Fe deposited in pyrite, is calculated as $F_{\text{py}} = f_{\text{py}} \times (1 - F_{\text{ox}})$. C) Pyrite data and contours of $F_{\text{ox}}/F_{\text{py}}$
 384 (relative size of oxic and pyrite sedimentary Fe sinks). Bold contours at 4 and 10 indicate
 385 thresholds for net O₂ source vs. sink behavior for volcanic H₂S/SO₂ inputs ratios of 1 (7) and 0 (8),
 386 respectively.



387 **Fig. 3**

388 D) F_{ox} and F_{py} , and molar O_2 yield estimates, from Monte Carlo error propagation. Violin plots for
 389 F_{ox} and F_{py} probability densities for results determined from propagation of errors on the $\epsilon^{56}Fe$
 390 and $\delta^{57}Fe$ values for each measured pyrite and the errors on the slopes of the MFLs (24). Blue
 391 filled (open) squares: Estimated molar O_2 yields per mole of pyrite buried for individual samples
 392 for H_2S/SO_2 input ratios of 1 (0). Blue (dashed) lines and shaded areas: mean molar O_2 yield for
 393 H_2S/SO_2 input ratios of 1 (0) and 95 % confidence interval for pyrites grouped by age interval.

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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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408 This PDF file includes:

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419 **Materials and Methods**

420 Methods

421 *Pyrite synthesis experiments*

422 To constrain the triple Fe isotopic expression of pyrite precipitation, pyrite was synthesized
423 at the University of Edinburgh, via the FeS-H₂S pathway following the methodology of Guilbaud
424 et al. (2011) (14) and references therein, which have consistently been demonstrated to produce
425 pyrite precipitates from an FeS_m (mackinawite) reactant. All reagents were of analytical grade, and
426 solutions were prepared using 18 MΩcm deionized water and sparged for 30 min with O₂-free
427 grade N₂ before use. Solutions were prepared and solid FeS_m was synthesized in N₂-filled
428 recirculating Saffron alpha anoxic chamber under O₂-free conditions. FeS_m was precipitated by
429 mixing 100 mL of 0.6 M iron (Fe²⁺) solution prepared with Mohr's salt ((NH₄)₂Fe(SO₄)₂·6H₂O;
430 Sigma Aldrich) with 100 mL of 0.6 M sulfide solution made with Na₂S·9H₂O (Sigma Aldrich).
431 This reaction produced a black precipitate. The precipitate was filtered using a Buchner filter with
432 Whatman™ No. 1 filter paper, resuspended in sparged water and the filtration was repeated three
433 times. The freshly precipitated FeS_m was freeze-dried overnight on a Mini-Lyotrap (LTE) freeze-
434 dryer then transferred back to the anoxic chamber and stored under O₂-free conditions until use.
435 The low-metal complexing MOPS (3-(N-morpholino)propanesulfonic acid) buffer (3-N-
436 morpholinopropanesulfonic acid, pK_a = 7.31, Fisher) was made by dissolution of its sodium salt
437 and in sparged water, buffered to pH 6 by NaOH titration. Ti³⁺ citrate was prepared by adding 5
438 mL 15% TiCl₃ to 50 mL 0.2 M Na citrate and buffered to pH 7 with Na₂CO₃. The solutions were
439 stored in the glove box under O₂-free conditions until use.

440 The pyrite precipitation experiments were prepared in the glove box. Approximately 300 mg
441 of the freeze-dried FeS_m was weighed into serum bottles, 10 mL of 0.05 M MOPS buffer solution
442 was added, and the bottles were sealed with rubber stoppers and aluminum crimper seals. The
443 sealed bottles were attached to a gas transfer manifold via a hypodermic needle inserted through
444 the rubber stopper, and the manifold and reaction bottle were flushed with O₂-free grade N₂ and
445 pumped down to -14 PSI (-97 kPa, at full vacuum) three times. A sealed serum bottle containing
446 800 mg solid Na₂S·9H₂O was attached to the manifold via a hypodermic needle and flushed and
447 pumped three times. A syringe was used to inject 2 mL of sparged, 50 vol% H₂SO₄ into the
448 Na₂S·9H₂O-containing bottle to generate H₂S. After H₂S transfer into the FeS_m-containing serum
449 bottle, the pressure was adjusted to slight under-pressure (~ -2.5 PSI or ~ -17 kPa) by N₂ addition.
450 The needle holes in the serum bottle septa were covered with silicone sealant and transferred to a
451 40°C oven to allow the pyrite precipitation reaction to take place. After different, pre-determined
452 reaction durations, the serum bottle reaction vessels were removed from the oven and frozen to
453 stop the reaction.

454 Once frozen, the serum bottles were unsealed under flushing N₂ and excess H₂S in the
455 headspace was removed. The bottles were then re-stoppered, the stoppers pierced with a
456 hypodermic needle under flushing N₂, and the bottles left in the freeze-dryer for a day. The freeze-
457 dried serum bottles were transferred to the anoxic chamber, and 2 mL sparged water and a few
458 drops of the Ti³⁺ citrate were added to poise the Eh at low negative values to prevent FeS_m
459 oxidation and ensure full dissolution of FeS_m in a preferential dissolution protocol developed by
460 Rickard et al. (2006) (36) and modified and calibrated by Guilbaud et al. (2011) (11). The serum
461 bottles were resealed and placed to a fume hood for preferential dissolution. In the fume hood, 20
462 mL of sparged 1.2 M HCl was injected into the serum bottle via hypodermic syringe to fully
463 dissolve only FeS_m and MOPS salt. Remaining solids, essentially pyrite, were separated by
464 filtering on a 0.45 μm Millipore filter, and rinsing with sparged water. The FeS_m in HCl solutions

465 were adjusted to 50 mL by addition of water and a 10 mL (20%) cut was dried down in clean
466 Savillex Teflon beakers for transport and isotopic analysis. Pyrite was dissolved with drops of
467 concentrated HNO₃, solutions were adjusted to 50 mL by addition of water and a 10 mL (20%) cut
468 was dried down in clean Savillex Teflon beakers for transport and isotopic analysis. A 20 mL cut
469 was taken for pyrite samples SB5 Py and SB6 Py, which were produced in short (4.66 hours)
470 duration experiments and for which low pyrite iron yields were anticipated. In the Origins
471 Laboratory at the University of Chicago, samples were dissolved in Aqua Regia with drops of 11
472 M HClO₄ at 140°C, and dried down twice, then treated three times with 2 mL of H₂O₂ to remove
473 organic carbon salts left in the FeS_m solutions by MOPS. The solutions were then re-dissolved in
474 5 mL 6M HCl ready for iron purification. A small (5 µL) aliquot of each solution was dried down
475 and redissolved in 0.3 M HNO₃ to check the iron concentration of these solutions using MC-ICP-
476 MS and determine the correct amount of volume of each sample solution to be passed through iron
477 purification.

478

479 *Analytical methods*

480 Analytical procedures for iron purification and isotopic measurements followed standard
481 procedures used at the Origins Laboratory at the University of Chicago (22, 37–40). Samples were
482 prepared from powders of black shale and IF material, and hand-picked pyrite grains. Sample
483 masses ranged from 12-22 mg, 2-6 mg, and 13-84 mg for black shale, IF, and pyrite grains
484 respectively. Samples were digested in clean Savillex Teflon beakers. First, 1 ml 28 M HF + 0.5
485 ml 15 M HNO₃ + a few drops 11 M HClO₄ was added, and closed beakers were heated at 130 °C.
486 Samples were evaporated to dryness and re-dissolved in Aqua Regia (0.75 ml 11 M HCl + 0.25
487 ml 15 M HNO₃) and a few drops 11 M HClO₄, before heating and evaporation was repeated. The
488 Aqua Regia + HClO₄ step was repeated 3 times to release all iron to solution. Samples were
489 evaporated to dryness and 0.5 ml of 6 M HCl or 10 M HCl was added, depending on the
490 purification procedure to be used. Larger volumes of the same acid were used for digestion of
491 pyrite grains, which contained greater masses of Fe. Iron purification made use of both the standard
492 ‘short column’ procedure, which is now routine in the Origins Laboratory (37, 40), and a ‘long
493 column’ procedure designed to more effectively eliminate Cu from the matrix (38, 39), which was
494 a concern for sulfide samples.

495 Short column iron purification: Disposable Bio-Rad Poly-Prep polyethylene columns were
496 filled with 1 ml of AG1-X8 200-400 mesh Cl-form anion exchange resin. The resin was pre-
497 conditioned with 10 ml of MilliQ H₂O, 5 ml of 1 M HNO₃, 10 ml of MilliQ H₂O, 9 ml of 0.4 M
498 HCl, 5 ml of MilliQ H₂O, and 2 ml of 6 N HCl. Samples were loaded onto columns in 0.25 ml of
499 6 M HCl. Matrix and interfering elements were eliminated by passing 8 ml of 6 M HCl through
500 the column. Iron was eluted with 9 ml of 0.4 M HCl and recovered in clean Teflon beakers.
501 Samples were evaporated to dryness and redissolved in 0.25 ml of 6 M HCl, before repeating the
502 column procedure a second time with new resin. All experimentally synthesized pyrite and FeS_m
503 samples were also purified using this procedure.

504 Long column iron purification: This alternative iron purification procedure was developed to
505 eliminate Cu as a potentially significant matrix element associated with sulfide phases. Reusable
506 30 ml Savillex Teflon columns with a 0.64 cm ID capillary cut to 10.5 cm length were loaded with
507 3 ml of AG1-X8 anion exchange resin. The resin was preconditioned with 10 ml MilliQ H₂O, 10
508 ml 0.4 M HCl, 5 ml MilliQ H₂O, 10 ml 0.4 M HCl, and 4 ml of 4 ml of 10 M HCl. Samples were
509 loaded onto columns in 0.25 ml of 10 M HCl. Matrix and interfering elements were eliminated by
510 passing 4.5 ml of 10 M HCl, and 30 ml of 4 M HCl, the latter to eliminate Cu in particular. Iron

511 was eluted with 9 ml of 0.4 M HCl and recovered in clean Teflon beakers. Samples were
 512 evaporated to dryness and redissolved in 0.25 ml of 10 M HCl, before repeating the column
 513 procedure with new resin.

514 Iron isotopic compositions were measured on a Neptune MC-ICP-MS at the University of
 515 Chicago. Analyses were made of the extent of isotopic fractionation (δ values), and the departure
 516 from a reference mass-dependent fractionation law (ϵ). The Fe isotopes at masses 54, 56, 57, and
 517 58 were measured simultaneously along with ^{53}Cr and ^{60}Ni for correction of ^{54}Cr and ^{58}Ni
 518 interferences on ^{54}Fe and ^{58}Fe respectively. The ^{53}Cr and ^{60}Ni interferences were corrected for
 519 using the exponential law. All of the Fe isotopes have molecular interferences with argide ions
 520 ($^{40}\text{Ar}^{14}\text{N}^+$, $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{16}\text{O}^1\text{H}^+$, and $^{40}\text{Ar}^{18}\text{O}^+$), which present a significant hindrance to obtaining
 521 the requisite precision to resolve mass-dependent fractionation laws. Therefore, measurements
 522 were made on the flat-topped peak shoulder in high-resolution mode using a standard Neptune
 523 entrance slit. A few sample analyses made use of ‘ultra-high-resolution mode’ utilizing the high-
 524 resolution mode of a Thermo Element 2 entrance slit. Results were consistent with those obtained
 525 using the standard HR method, but offered no improvement in precision whilst requiring higher
 526 iron concentrations to obtain the same signal. Nickel or aluminum sampler and H skimmer cones
 527 were used. Standard-sample bracketing was used to correct isotopic ratio measurements for
 528 instrumental mass fractionation, and Fe isotopic ratios of samples are reported relative to the
 529 average isotopic ratios of the bracketing standard solutions of IRMM-524, which has an identical
 530 isotopic composition to IRMM-014. The exponential law was initially used to calculate ϵ values
 531 by fixing $^{57}\text{Fe}/^{54}\text{Fe}$ to 0.362549, the value of IRMM-014. The δ and ϵ values of samples are given
 532 by

$$533 \quad \delta = \left[\left(\frac{i\text{Fe}/^{54}\text{Fe}}{\text{sample}} / \left(\frac{i\text{Fe}/^{54}\text{Fe}}{\text{std}} \right) - 1 \right] \times 10^3,$$

$$534 \quad \epsilon = \left[\left(\frac{i\text{Fe}/^{54}\text{Fe}}{\text{sample}}^* / \left(\frac{i\text{Fe}/^{54}\text{Fe}}{\text{std}} \right)^* - 1 \right] \times 10^4,$$

535 where $i = 56, 57,$ or 58 and the $*$ indicates ratios corrected for mass fractionation by internal
 536 normalization to a fixed reference $^{57}\text{Fe}/^{54}\text{Fe}$ ratio using the exponential law (17, 20),

$$537 \quad \ln \left(\frac{i\text{Fe}/^{54}\text{Fe}}{\text{sample, corrected}} \right)^* = \ln \left(\frac{i\text{Fe}/^{54}\text{Fe}}{\text{sample, measured}} \right) - \ln \frac{\left(\frac{^{57}\text{Fe}/^{54}\text{Fe}}{\text{sample, measured}} \right) \ln \left(\frac{m_{i\text{Fe}}/m_{^{54}\text{Fe}}}{m_{^{57}\text{Fe}}/m_{^{54}\text{Fe}}} \right)}{\left(\frac{^{57}\text{Fe}/^{54}\text{Fe}}{\text{fixed reference}} \right) \ln \left(\frac{m_{^{57}\text{Fe}}/m_{^{54}\text{Fe}}}{m_{^{54}\text{Fe}}/m_{^{54}\text{Fe}}} \right)}$$

538 Bracketing standards are also internally normalized using the same exponential law.
 539 Subsequent to measurements, data were renormalized to the high-temperature equilibrium limit
 540 law for display, to fit the common convention used with other isotope systems. Data normalized
 541 to the exponential law are also presented in Tables S1 and S2, and a version of Figure 1B using
 542 this normalization is also presented in Figure S1.

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

553 For experimentally synthesized samples, the mass-dependent Fe isotopic fractionation ($\delta^{56}\text{Fe}$)
554 was also determined by standard Fe isotopic analytical methods. A quartz cyclonic spray chamber
555 was used to introduce 1 ppm solutions into the Neptune operating in medium resolution mode,
556 resulting in a signal of ~ 7 V. Isotopic compositions were determined by standard-sample
557 bracketing. All Fe isotopic analyses of experimentally synthesized samples (both triple isotopic
558 and conventional) were normalized to IRMM-524 during analyses, but subsequently renormalized
559 to the measured isotopic compositions of the starting batches of FeS_m material used in respective
560 experiments. All errors were combined in quadrature as appropriate. The average fractionation
561 factor we determined for the pyrite precipitation reaction was $\alpha_{\text{FeS-pyrite}} = 1.0023 \pm 0.0003$ (95%
562 C.I.), consistent with the results of Guilbaud et al. (2011) (14). This fractionation factor was
563 determined by calculating the average difference between the FeS_m and pyrite splits from each
564 serum bottle experiment. The degree of pyritization (DOP – the fraction of the total Fe in the pyrite
565 pool) was calculated from the total iron masses in each split indicated by concentration
566 measurements and known dilution factors. The low DOP values (max ~ 14 %) obtained in our
567 experiments were not conducive to fitting the data to a Rayleigh distillation trend, however the
568 distance between linear trends plotted through $\delta^{56}\text{Fe}$ vs. degree of pyritization for the FeS_m and
569 pyrite data also gave an average fractionation factor of $\alpha_{\text{FeS-pyrite}} = 1.0023$ (Fig. S2).

570 We saw no systematic difference between short and long column purification techniques in
571 triple Fe isotopic data for IF sample JD-C165A, and pyrite sample SF-1 599.8 Py, which were
572 each processed multiple times using either column procedure to check the reproducibility of our
573 measurements in the absence of geostandard materials, which have been analyzed to this level of
574 precision (Fig. S2). In all cases, the individual pyrite analyses for this repeat sample have $\epsilon^{56}\text{Fe}$
575 values that significantly more positive than the value of the anticipated for IF with the same $\delta^{57}\text{Fe}$
576 value (Fig. S2). In addition, as a check for possible matrix effects in the preparation of IF and
577 pyrite samples, we performed a matrix test with IRMM-524 standard iron solution. Briefly,
578 aliquots of an IF sample (REX 187.5) and a pyrite sample (SF-1 623.6 Py) were passed through
579 the short column purification procedure and the eluted matrix from each was collected. These
580 matrix cuts were further purified by being passed through this column chemistry procedure again.
581 These matrix cuts were mixed with a solution of IRMM-524 back to the original iron
582 concentration, and the iron was purified with two passes on short columns in the same manner as
583 other samples. The $\epsilon^{56}\text{Fe}$ values of both matrix-adjusted solutions and a pure solution of IRMM-
584 524 were within error of zero and all identical within error (Fig. S2), suggesting that sample
585 matrices did not systematically affect our $\epsilon^{56}\text{Fe}$ analyses.

586

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

588 Triple Fe isotopic systematics allow the isotopic composition of any given isotopically
589 depleted pyrite to be deconvolved into contributions from KIE during pyrite precipitation, and
590 isotopic depletion in dissolved Fe^{2+} resulting from the removal of isotopically heavy Fe^{3+}
591 (oxyhydr)oxides. Rough estimates for those contributions can be solved graphically (Fig. 2A),
592 however the uncertainty on those estimates requires propagation of all uncertainties on both the
593 KIE and oxidation MFLs, in addition to uncertainty of individual pyrite measurements. This error
594 propagation was performed using a Monte Carlo method in a MATLAB script.

595 For each pyrite and IF datapoint, an array of simulated datapoints was generated by randomly
596 sampling 1000 times from a normal distribution defined by the 95 % C.I. of the measured $\epsilon^{56}\text{Fe}$
597 and $\delta^{57}\text{Fe}$ values and standard deviations. From the 1000 sets of randomly generated IF datapoints,
598 1000 MFLs were generated by linear regression to encompass the anticipated range of seawater

599 Fe²⁺ evolutions in $\epsilon^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$ space that could be driven by Fe³⁺ (oxyhydr)oxide removal. An
 600 array of 1000 values for the kinetic slope was generated by randomly sampling 1000 times from a
 601 normal distribution defined by the 95 % C.I. of the experimentally determined slope. The intercept
 602 of a line with the kinetic slope passing through the pyrite $\epsilon^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$, with the MFL fitted to
 603 the IF data, was found by solution of simultaneous equations (Fig. S4). The IF line, and the line
 604 defining the KIE trajectory which connects pyrite datapoints to the IF line, are given respectively
 605 by the equations:

$$606 \quad \epsilon^{56}\text{Fe} = a_{\text{ox}}\delta^{57}\text{Fe} + b_{\text{ox}}$$

$$608 \quad \epsilon^{56}\text{Fe} = a_{\text{KIE}}\delta^{57}\text{Fe} + b_{\text{KIE}}$$

609
 610 where a is the empirically determined slope of the MFL, and b is the intercept with the vertical
 611 axis. For known $\epsilon^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values of a given pyrite, the second equation can be rearranged
 612 as:

$$613 \quad b_{\text{KIE}} = \epsilon^{56}\text{Fe}_{\text{py}} - a_{\text{KIE}}\delta^{57}\text{Fe}_{\text{py}}$$

614 The intercept with the IF MFL is then found by equating the line equations, giving (after
 615 substitution):

$$616 \quad \delta^{57}\text{Fe}_{\text{int}} = \frac{(\epsilon^{56}\text{Fe}_{\text{py}} - a_{\text{KIE}}\delta^{57}\text{Fe}_{\text{py}} - b_{\text{ox}})}{(a_{\text{ox}} - a_{\text{KIE}})}$$

617 where the subscript _{int} refers to the value at the intercept (note in the main text this is denoted
 618 with the subscript _{wo}) (Fig. S4). The $\delta^{57}\text{Fe}$ value at the intercept with the IF MFL ($\delta^{57}\text{Fe}_{\text{int}}$) was
 619 taken as the isotopic composition of the pyrite-forming water mass that had already undergone
 620 iron oxidation, and the magnitude of the KIE during pyritization was calculated as the difference
 621 between the intercept value and the $\delta^{57}\text{Fe}$ of pyrite. This exercise was repeated 1000 times for
 622 each depleted pyrite sample using the randomly generated values of all parameters described. We
 623 note that in the Main Text, the discussion focusses on $\delta^{56}\text{Fe}$ values as these are more commonly
 624 reported in the literature, but here the exact procedure is detailed as performed, and conversion
 625 between $\delta^{57}\text{Fe}$ and $\delta^{56}\text{Fe}$ values is done by dividing by the values of $\theta^{56/57}$ presented in this study.

626 The extent of Fe²⁺ oxidation (F_{ox}) to give a certain $\delta^{57}\text{Fe}_{\text{int}}$ was calculated using a Rayleigh
 627 distillation model:

$$628 \quad \delta^{57}\text{Fe}_{\text{int}} = \delta^{57}\text{Fe}_i + 1000(\alpha - 1) \ln(1 - F_{\text{ox}})$$

629 where α is the fractionation factor during in Fe²⁺ oxidation and precipitation that gives
 630 fractionation $1000 \times (\alpha - 1) = 0.5 \text{ ‰/amu}$ during Fe³⁺ (oxyhydr)oxide removal (16), the subscript _i
 631 denotes the starting $\delta^{57}\text{Fe}$ for a hydrothermal Fe²⁺ source of $\sim -0.3 \text{ ‰}$ (9, 41). Iterations where the
 632 inferred $\delta^{57}\text{Fe}$ of seawater was more positive than this value were rejected as they would imply a
 633 negative degree of Fe²⁺ oxidation.

634 The fraction of pyrite precipitation (F_{py} in Main Text) was also determined in a Rayleigh
 635 distillation model. We calculate f_{py} by assuming that bulk pyrite nodules represent the cumulative
 636 product of pyrite precipitated from the initial Fe²⁺ pool. This contrasts with in situ measurement
 637 of individual nodule layers that better approximate instantaneous precipitate compositions during
 638 the growth of pyrite grains (17, 18). The magnitude of the KIE that was expressed in the product
 639 was calculated as the difference between the product and initial reactant:

$$640 \quad \delta^{57}\text{Fe}_{\text{py}} - \delta^{57}\text{Fe}_{\text{int}} = \frac{(F_{\text{py}} - 1) \times 1000(\alpha - 1) \ln(1 - F_{\text{py}})}{F_{\text{py}}}$$

641 where we assumed the maximum fractionation during pyrite precipitation (via FeS_m) from
642 Fe^{2+} of $1000 \times (\alpha - 1) = -1.55$ ‰/amu. Iterations requiring a larger instantaneous fractionation were
643 rejected. The value of F_{py} was determined by solving this equation numerically. The cumulative
644 product composition cannot evolve past the initial composition of the reactant reservoir, when the
645 reactant reservoir has been completely consumed. Therefore, iterations requiring a positive offset
646 of the pyrite datapoint from $\delta^{57}\text{Fe}$ of seawater were rejected. Once the 1000 iterations for
647 calculation of F_{ox} , and F_{py} , had been completed, the fractional size of the sulfidic sink (F_{ss} in Main
648 Text) was calculated as $F_{\text{py}} \times (1 - F_{\text{ox}})$ for each pyrite with a confidence interval dictated by the
649 range of values generated in the 1000 iterations. Monte Carlo simulation estimates of F_{py} and F_{ox}
650 for each pyrite sample spanned a large range, but these variations were strongly correlated
651 (Fig. S5). This is because a more negative estimate for the isotopic composition of seawater (which
652 implies a larger F_{ox}), gives a smaller estimate for the fractionation during the precipitation of pyrite
653 from the oceanic iron pool (which implies a larger F_{py}). These two effects have an opposite impact
654 on the estimate of F_{ss} , therefore, F_{ss} estimates vary less than F_{ox} or F_{py} .

655 Triple-Fe-isotope-derived F_{ox} and F_{py} from pyrites can also be used to estimate the relative
656 fluxes of Fe^{2+} and S (as SO_4^{2-} , H_2S , and S_8) to shelf environments in the Neoproterozoic and pre-GOE
657 Paleoproterozoic. Assuming an FeS_2 stoichiometry for sedimentary sulfide, the Fe/S ratio in the
658 shelf sediments is given by $(\text{Fe}/\text{S})_{\text{sed}} = [F_{\text{py}} + F_{\text{ox}}]/[2 \times F_{\text{py}}]$, where F_{py} and F_{ox} are calculated based
659 on the triple-Fe-isotopic measurements presented above. We only consider the relative magnitude
660 of oxide and sulfide iron sinks (e.g., iron silicates or carbonates are not considered) because they
661 are the only ones that have large known isotopic effects, and that can influence redox balance in
662 the Archean. Central estimates of $(\text{Fe}/\text{S})_{\text{sed}}$ have a range of 0.7 to 2.0 across all samples (Table S4).
663 The Jeerinah and Lokammona formation pyrites have $(\text{Fe}/\text{S})_{\text{sed}} \geq 1.3$, while younger pyrites
664 deposited shortly before the GOE have lower ratios. For comparison, the ratio of modern Fe input
665 from continental weathering (0.4 Tmol/yr) and hydrothermal venting at mid-ocean ridges (0.18
666 Tmol/yr) (42), to subaerial volcanic SO_2 emissions (0.4-1.4 Tmol/yr) (3), continental weathering
667 supply of SO_4^{2-} (11 Tmol/yr) (42), and hydrothermal H_2S supply (0.17 Tmol/yr) (42), is
668 approximately 0.05. The Neoproterozoic-Paleoproterozoic pyrite record thus suggests a ratio of Fe to
669 S supply to the oceans 14-40 times greater than modern. Archean hydrothermal and continental
670 Fe^{2+} fluxes exceeded modern levels, due to higher mantle heat flow (42), low sulfate content in
671 the ocean (43), and continental weathering in contact with anoxic atmosphere. On another hand,
672 the weathered SO_4^{2-} flux and hydrothermal H_2S flux (43) were lower throughout the Archean. Our
673 calculated $(\text{Fe}/\text{S})_{\text{sed}}$ values do not necessarily require weaker Archean volcanic SO_2 fluxes than
674 now, but they indicate that locally developed euxinic conditions (3, 4, 8) are not representative of
675 the global ocean iron cycle where the burial of Fe^{3+} -(oxyhydr)oxides was the dominant iron sink.
676 For ca. 2.5 Ga pyrites, an additional source of sulfate from oxidative weathering of continental
677 sulfides (4) might explain why $(\text{Fe}/\text{S})_{\text{sed}}$ values are lower relative to those in the older Jeerinah and
678 Lokammona formations (Table S4).

679

680 Sample Materials

681 Geological setting and age constraints for shale-hosted pyrite samples are given by Rouxel et
682 al. (2005) (6). Ages and geological units for all samples in this study are provided in Table S3.
683 References for age constraints for pyrite and shale samples, and most IF samples, are provided in
684 Rouxel et al. (2005; 2006) (6, 23), and Planavsky et al. (2012) (7), respectively. Age data for
685 samples from the Hotazel Formation and Isua Supracrustal Belt IFs are provided by Gumsley et

686 al. (2017) (2), and Moorbath et al. (1973) (44), and the geologic setting and Fe isotopic systematics
687 of these IF have been discussed in the literature elsewhere (25, 45, 46).

688 Pyrite grains from organic rich shales, a few bulk organic rich shales, and bulk IF samples
689 were selected for this study. Pyrite grains and bulk shales were sampled from a subset of drill core
690 samples previously studied for Fe isotopic variations by Rouxel et al. (2005; 2006) (9, 26), New
691 pyrite grains were picked at the University of Hawaii. The nature of these grains was described in
692 detail by Rouxel et al. (2005) (6). Pyrite grains in organic-rich shales that were subsampled in our
693 study occurred as nodules ~ 1 mm to 1 cm in diameter, with C-rich inclusions in variable amounts.
694 The nodular pyrite either had no internal structure, or was composed of concentrically laminated,
695 fine-grained pyrite or bladed pyrite crystals. Euhedral pyrite crystals commonly overgrew the outer
696 part of the nodules. Shale lamina typically bends around pyrite nodules, which supports
697 interpretations of their origins as being formed early on during diagenesis. Pyrite nodules often
698 display complex features such as multiple-growth bands or composite nodules formed by
699 coalescence of several nodules. Dissolution and reprecipitation of primary sulfide nodules could
700 have happened in some samples and likely resulted in formation of massive pyrite, often
701 characterized by euhedral grains free of C-rich inclusions.

702 Localized dissolution-reprecipitation is unlikely to have affected Fe-isotopic compositions of
703 pyrites. In the large numbers of samples analyzed per formation by Rouxel et al. (2006) (9) strongly
704 negative $\delta^{56}\text{Fe}$ values were a consistent feature and no link between Fe isotopic composition and
705 the nature of individual pyrite grains was reported, which supports the notion that these are primary
706 sedimentary signatures and not the results of later alteration of the host rocks. Heard and Dauphas
707 (2020) (11) recently discussed the fidelity of the pyrite Fe isotope record as an archive of primary
708 sedimentary signatures. In brief, the resistance of this system to metamorphic overprinting due: to
709 the high abundance of Fe, low solubility of pyrite and small size of Fe isotopic fractionations at
710 metamorphic temperatures all make it unlikely that primary sedimentary Fe isotopic signatures
711 have been compromised by secondary processes that may nonetheless have affected the texture of
712 pyrite grains. In practice, Marin-Carbonne et al. (2020) (18) recently demonstrated through in situ
713 work that Archean pyrites that experienced late fluid circulation that led to partial recrystallization
714 and alteration of S isotopic systematics, did not modify the Fe isotopic composition, in line with
715 our expectations outlined above.

716

717 **Supplementary Text**

718 Background on mass fractionation laws for Fe isotopes

719 *Instantaneous fractionations*

720 Numerous reaction pathways have been proposed to create the $>4\text{‰}$ $\delta^{56}\text{Fe}$ range in Archean
721 IFs, shales, and pyrites. The extent of Fe isotopic fractionation is insufficient to discriminate
722 between different scenarios for sedimentary iron cycling in the Archean oceans, because many
723 fractionation processes can generate a large and indistinguishable range in delta values.
724 Considering two isotopic ratios could resolve this ambiguity, because the slope of $\delta^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$
725 reflects the mass fractionation law (MFL) governing a process, and this law may be distinct for
726 the fractionation processes at the root of various scenarios proposed for the Archean Fe isotopic
727 record. Mass-dependent fractionation is described with a power law

$$728 \quad {}^{56}\alpha_{A/B} = {}^{57}\alpha_{A/B}^{\theta^{56/57}}$$

729 where ${}^x\alpha_{A/B}$ are fractionation factors for isotope x between reservoirs A and B, and ${}^{56/57}\theta$ is
730 the mass dependent exponent or slope in triple Fe isotope space (20). Natural processes imparting

731 different slopes of MFLs in three-isotope diagrams have been identified for O (47–50), Mg (19,
 732 51), S (52–54), Ca (55), Ti (55), and Fe (21, 22), but this has yet to be investigated for Fe isotopes
 733 in sedimentary rocks with sufficient precision to resolve distinct slopes. The slope $\theta^{56/57}$ for the
 734 triple-Fe-isotope diagram is given by

$$735 \quad \theta^{56/57} = \frac{\delta'^{56}\text{Fe}}{\delta'^{57}\text{Fe}} = \frac{\ln\left(\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right) / \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{std}}\right)}{\ln\left(\left(\frac{^{57}\text{Fe}}{^{54}\text{Fe}}\right) / \left(\frac{^{57}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{std}}\right)},$$

736 where δ' is related to the standard δ notation by

$$737 \quad \delta' = 1000 \times \ln((\delta/1000) + 1).$$

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

$$741 \quad \epsilon'^{56}\text{Fe} = [\delta'^{56}\text{Fe} - 0.672 \times \delta'^{57}\text{Fe}] \times 10.$$

742 In $\epsilon'^{56}\text{Fe}$ vs. $\delta'^{57}\text{Fe}$ diagrams MFLs are straight lines, and when the high-temperature
 743 equilibrium limit law with $\theta^{56/57} = 0.678$ is used as the reference law, $\epsilon'^{56}\text{Fe}$ values are 0 if
 744 fractionation follows the exponential law. Other MFLs have positive (negative) slopes if $\theta^{56/57}$ is
 745 larger (smaller) than 0.678.

746 These laws describe mass-dependent fractionation in a single step process. This approach is
 747 an oversimplification in cases where isotopes have been fractionated via several geochemical
 748 pathways, via Rayleigh distillation, or where samples reflect mixtures of two (or more) isotopically
 749 distinct pools of the element of interest. These concerns are well-documented in the more mature
 750 field of triple O and S isotope study (47–49, 52–54), but we show here that these concerns are of
 751 diminished importance in application to low-temperature Fe isotope systematics. This is because
 752 both Rayleigh distillation and mixing produce curves in $\epsilon'^{56}\text{Fe}$ vs. $\delta'^{57}\text{Fe}$ space that are practically
 753 indistinguishable from instantaneous MFLs over the natural range of Fe isotopic variations.

754

755 *Rayleigh distillation*

756 In the case of Rayleigh distillation, Ono *et al.* (53) have shown that the closed-system
 757 evolution of a reactant reservoir (A) during formation of a product (B) results in an observed slope
 758 in three-isotope space for A that is distinct from the intrinsic slope of the instantaneous
 759 fractionation process (Fig. S3A). In this study, the evolution of the reactant reservoir corresponds
 760 to the generation of an isotopically light Fe^{2+} pool through the removal of an isotopically heavy
 761 Fe^{3+} oxide product. The evolution of the reactant, written in δ' notation, is

$$762 \quad \delta'^x\text{Fe}_A = ({}^x\alpha - 1) \times \ln({}^{54}f_A) \times 1000 + \delta'^x\text{Fe}_{A,i},$$

763 where $\delta'^x\text{Fe}_{A,i}$ is the initial isotopic composition of the reactant, $\delta'^x\text{Fe}_A$ is the isotopic
 764 composition of the reactant when a fraction ${}^{54}f_A$ of the reactant A remains, and ${}^x\alpha$ is the isotopic
 765 fractionation factor for isotope x in the reaction of A to form product B. In three isotope space, the
 766 isotopic composition of the reactant will evolve with an effective slope, $\theta^{56/57}_{\text{eff}}$

$$767 \quad \theta^{56/57}_{\text{eff}} = \frac{\delta'^{56}\text{Fe}_A - \delta'^{56}\text{Fe}_{A,i}}{\delta'^{57}\text{Fe}_A - \delta'^{57}\text{Fe}_{A,i}} = \frac{({}^{56}\alpha - 1) \times \ln({}^{54}f_A)}{({}^{57}\alpha - 1) \times \ln({}^{54}f_A)} = \frac{{}^{57}\alpha^{\theta^{56/57}_{\text{inst}} - 1}}{{}^{57}\alpha - 1},$$

768 where $\theta^{56/57}_{\text{inst}}$ is the intrinsic slope for the instantaneous reaction. The distinctions between
 769 θ_{inst} and θ_{eff} are significant in the O and S isotope systems, where fractionations and relative
 770 isotopic mass differences are large. In the case of Fe isotopes, specifically Rayleigh distillation of

771 aqueous Fe²⁺ driven by oxidation and removal of Fe³⁺ minerals, the relevant values for $\theta^{56/57}_{\text{inst}}$ and
 772 $^{57}\alpha$ are 0.678 and on the order of 1.0015 respectively (14). Inserting these values results in
 773 $\theta^{56/57}_{\text{eff}} \approx 0.6778$, which is smaller than the intrinsic slope by only 0.0002 and not resolvable from
 774 the intrinsic slope for any naturally occurring range of fractionations (Fig. S3A). Nie *et al.* (22)
 775 provided a slightly different relation between the effective and intrinsic slopes for UV photo-
 776 oxidation, with $^{56}\alpha = 1.0012$, and determined the same result, that the effective slope for the
 777 evolving reactant reservoir was smaller than the instantaneous slope by just 0.0002 and thus the
 778 two slopes were indistinguishable within current measurement uncertainties. These calculations
 779 imply that discussing theoretical, single-step MFLs is an appropriate approximation for the
 780 evolution in triple Fe isotope space of an Fe²⁺ reservoir affected by oxidation and removal of Fe³⁺
 781 products.

782 783 *Mixing*

784 Unlike fractionation processes, mixing lines are non-linear in logarithmic coordinates for
 785 isotopic ratios (Fig. S3B), so another pertinent question for this study is the degree to which $\epsilon^{56}\text{Fe}$
 786 *vs.* $\delta^{57}\text{Fe}$ data may be explained by mixing systematics rather than distinct intrinsic MFLs. We
 787 define two isotopic reservoirs A and B as endmembers in a mixing array, and for the sake of
 788 simplicity (though this is not required), describe the linear tie-line between these two points as an
 789 instantaneous mass fractionation with the intrinsic slope and fractionation factors $\theta^{56/57}_{\text{inst}}$ and $\alpha_{A/B}$,
 790 respectively. Following Ono *et al.* (53) the magnitude of the effect of mixing on $\epsilon^{56}\text{Fe}$ values is
 791 given as

$$792 \epsilon^{56}\text{Fe}_{\text{mix}} - \epsilon^{56}\text{Fe}_{\text{MFL}} = \left[\ln \left(^{54}f_A \left(^{57}\alpha_{A/B} \theta^{56/57}_{\text{inst}} - 1 \right) + 1 \right) - \right. \\ 793 \left. \theta^{56/57}_{\text{inst}} \times \ln \left(^{54}f_A \left(^{57}\alpha_{A/B} - 1 \right) + 1 \right) \right] \times 10,000,$$

794 where $\epsilon^{56}\text{Fe}_{\text{mix}}$ and $\epsilon^{56}\text{Fe}_{\text{MFL}}$ refer to the points on the mixing curve and the MFL connecting
 795 A and B, respectively, and $^{54}f_A$ is the fraction of ^{54}Fe from A in the mixture. For $\epsilon^{56}\text{Fe}$ *vs.* $\delta^{57}\text{Fe}$
 796 coordinates, this mixing curve is concave upward (Fig. S3B), analogous to the familiar example
 797 of $\Delta^{33}\text{S}$ *vs.* $\delta^{34}\text{S}$. When the most highly fractionated value in the Archean dataset, $\delta^{57}\text{Fe} \approx -5$ ‰,
 798 is used as the endmember mixing with another endmember at $\delta^{57}\text{Fe} = 0$ ‰, the maximum
 799 difference between $\epsilon^{56}\text{Fe}_{\text{mix}}$ and $\epsilon^{56}\text{Fe}_{\text{MFL}}$ is 0.0069 (Fig. S3B), which is an order of magnitude
 800 smaller than typical analytical precision for measurement of these values and hence they are
 801 unresolvable. Therefore, while mixing lines in these coordinates are not strictly linear, in practice
 802 they are very well approximated by straight lines and our data cannot be explained through non-
 803 linear mixing of endmembers lying on a single MFL.

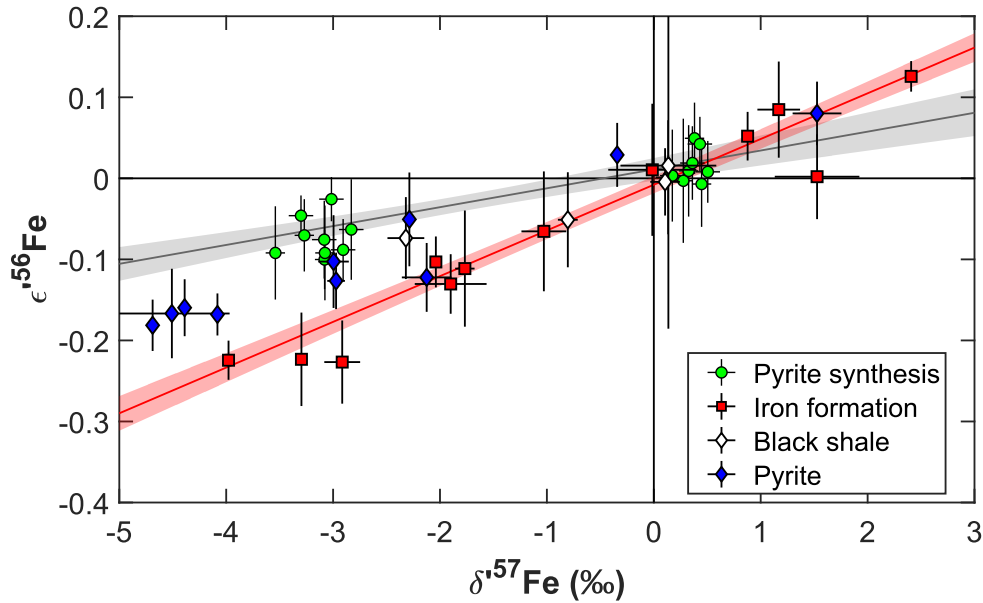
804 805 *Iron isotope MFLs*

806 Mass-dependent triple-Fe-isotopic systematics have been explored in few publications to
 807 date, and only once previously in the context of low temperature aqueous geochemistry. Nie *et al.*
 808 (22) determined $\theta^{56/57} = 0.6785 \pm 0.0009$ associated with UV photo-oxidation of dissolved Fe²⁺ in
 809 anoxic solutions at near-neutral pH. A high precision measurement of the ca. 3.83 Ga IF-G
 810 geostandard from an IF in Isua, Greenland has $\epsilon^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ consistent with isotopically heavy
 811 ferric precipitates from those experiments (22) and both are within error of the high-temperature
 812 limit equilibrium law with $\theta^{56/57} = 0.678$. However, the magnitude of isotopic enrichment in IF-G
 813 and isotopically heavy IF oxides in general provide insufficient leverage in three-isotope space to
 814 distinguish different MFLs at the available precision for $\epsilon^{56}\text{Fe}$. Whether different iron oxidation
 815 pathways for IF formation do have distinct MFLs has not yet been tested experimentally. However,

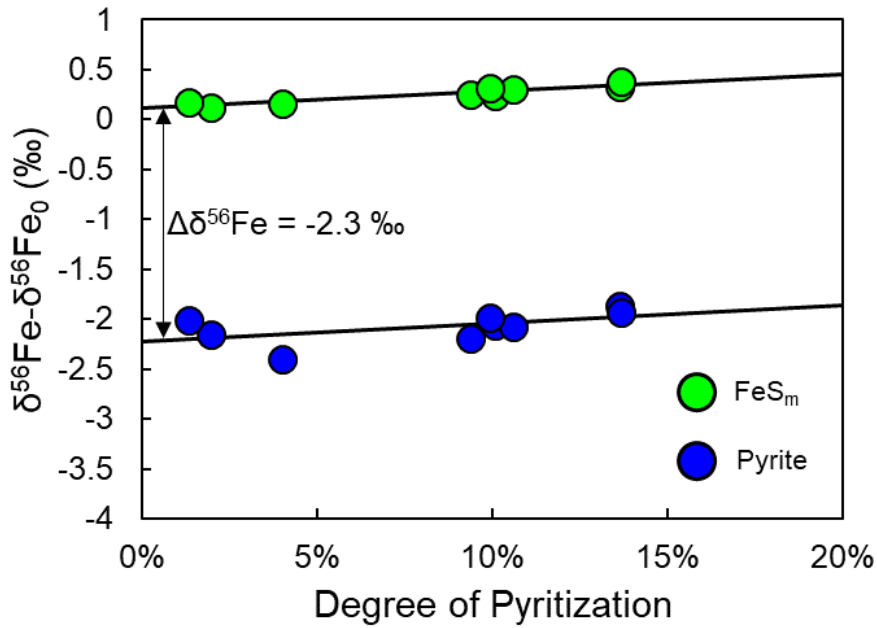
816 the fact that the high temperature equilibrium law, the MFL for photo-oxidation, and our observed
817 MFL defined by IFs including Hotazel Mn-IF samples, which were most likely fractionated by
818 direct O₂ oxidation (25), are all within error of one another suggests that fractionations of Fe
819 isotopes driven by Fe²⁺-Fe²⁺ equilibration may follow the equilibrium MFL regardless of the
820 oxidation process involved. It will be important for future studies to constrain the value of $\theta^{56/57}$
821 for the remaining proposed oxidation pathway for IF, anoxygenic photoferrotrophy (56, 57),
822 however our results to date suggest it is unlikely that triple Fe isotopic systematics will be able to
823 identify the oxidation pathway for IF due to the tendency of Fe²⁺ and Fe³⁺ to rapidly isotopically
824 equilibrate.

825 Precipitation of pyrite is a kinetically controlled process associated with a large kinetic
826 isotope effect (KIE) that enriches early precipitates in the light isotopes of Fe (14, 15). The slope
827 $\theta^{56/57}$ is anticipated to be shallower than that of equilibrium isotope fractionation (19, 20), an
828 expectation borne out in triple Fe isotopic measurements of olivine phenocrysts affected by iron
829 diffusion (21). However, the value of $\theta^{56/57}$ relevant to pyrite precipitation did not have an
830 empirical constraint prior to our study. Our pyrite precipitation experiments resulted in maximum
831 DOP of ~14% (Fig. S2). By mass balance most iron was always left in the FeS_m pool and large
832 fractionations from the starting composition of the experiment were observed in the pyrite pool,
833 which provides leverage to determine the slope of the instantaneous MFL associated with pyrite
834 precipitation. Our triple Fe isotopic analysis was consistent with a single kinetic MFL, with a slope
835 of 0.0233 ± 0.0057 in $\epsilon^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$ space, which translates to a slope $\theta^{56/57}_{\text{KIE}} = 0.6743 \pm 0.0006$.
836 This is much shallower slope than that of the equilibrium limit law associated with redox
837 equilibrium, but steeper than the exponential kinetic law that describes pure atomic transport (19,
838 20).

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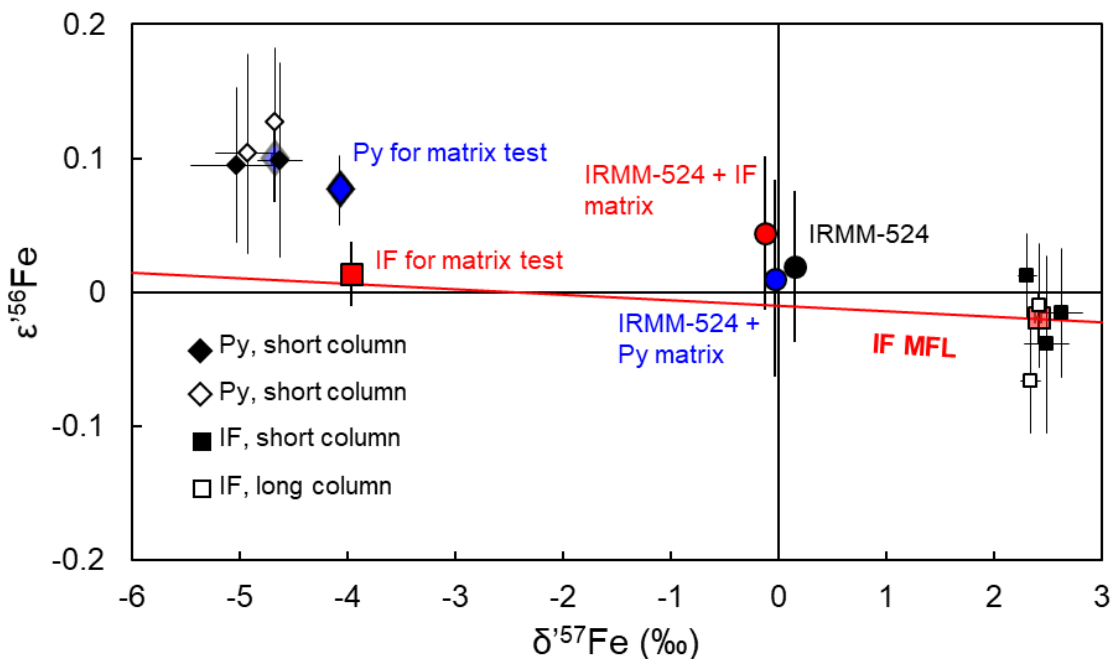
843 **Fig. S1.**
844 Triple-Fe-isotope systematics for IFs, pyrites, and black shales in $\epsilon^{56}\text{Fe}$ vs. $\delta^{57}\text{Fe}$ space,
845 normalized to the exponential law. Error bars and envelopes are 95% confidence intervals. The
846 slopes of endmember MFLs associated with iron-redox processes, and KIEs during pyritization,
847 are constrained through analysis of isotopically light Mn-rich IFs and laboratory pyrite
848 precipitation via the H_2S pathway (14, 24, 35), respectively. The slope of the IF MFL agrees with
849 the theoretical equilibrium law, implying control by Fe^{2+} - Fe^{3+} equilibrium (20, 22). Pyrite
850 synthesis defines a kinetic MFL for pyrite precipitation. Pre-GOE pyrites fall in an intermediate
851 space between redox equilibrium and kinetic endmembers.
852
853



854 **Fig. S2.**

855 Iron isotopic fractionation between FeS_m and pyrite during abiotic precipitation of pyrite. The
 856 average Fe isotopic fractionation between FeS_m and pyrite, a shift in $\delta^{56}\text{Fe}$ of -2.3 ‰, is
 857 determined both through taking the average difference between the two phases in individual
 858 experiments, and through the distance between linear fits of $\delta^{56}\text{Fe}$ vs. degree of pyritization. Low
 859 degrees of pyritization resulted in limited distillation of the reactant FeS_m reservoir poorly suited
 860 to determining a fractionation factor assuming Rayleigh distillation.

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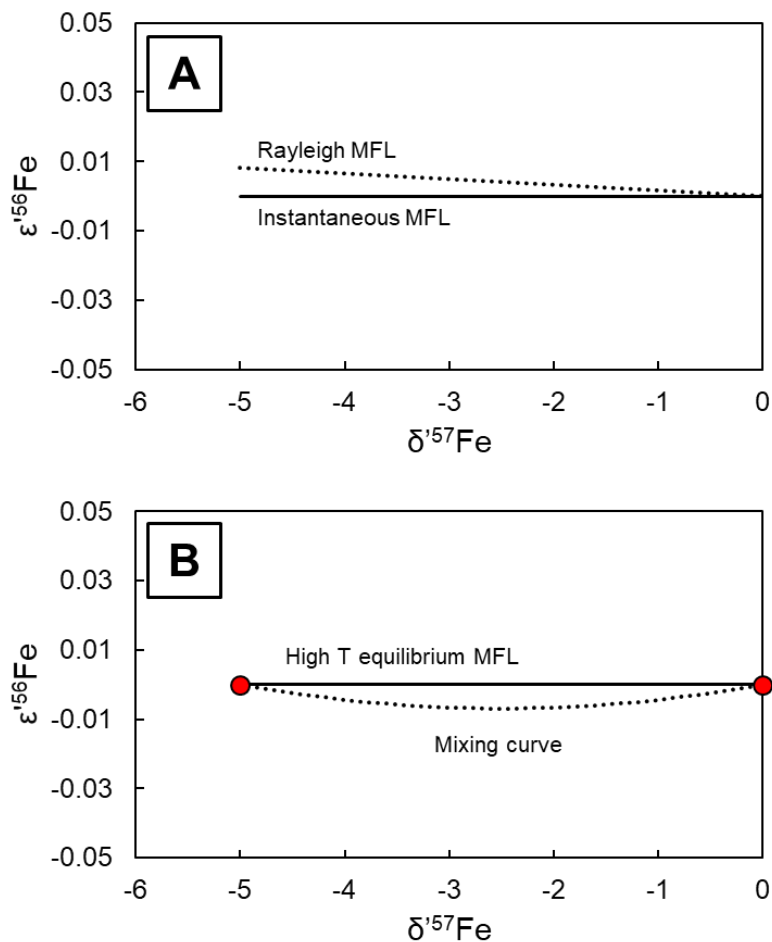


862

863 **Fig. S3.**

864 Tests performed on triple Fe isotopic analyses. Purification and analysis of replicate aliquots of IF
 865 sample JD-C 165A and pyrite sample SF-1 599.8 Py performed using short column (black filled
 866 symbols) and long column (open symbols) chromatography procedures, with average values for
 867 each sample shown in the pale colored symbols in the background. Despite some analytical scatter,
 868 we see no significant or systematic effect of using one purification procedure over another, and all
 869 replicate pyrite analyses were distinct from the triple Fe isotopic composition one would expect
 870 for a sample that was fractionated solely by the redox processes driving the IF MFL. Matrix mixing
 871 tests performed with IRMM-524 and matrix from IF sample REX 187.5 (bold red square) and
 872 pyrite sample SF-1 623.6 Py (bold blue diamond) revealed no resolvable matrix effect on $\epsilon'^{56}\text{Fe}$
 873 analysis, with the pure IRMM-524 solution (black circle), IF matrix IRMM-524 solution (red
 874 circle), and pyrite matrix IRMM-524 solution (blue circle) all having $\epsilon'^{56}\text{Fe}$ values which are
 875 within error of one another and zero. Note that if matrix effects drove the difference between pyrite
 876 and IF triple Fe isotope variations, the IRMM-524 sample doped with pyrite matrix would need to
 877 have significantly more positive $\epsilon'^{56}\text{Fe}$ than the IF-doped standard, and it does not.

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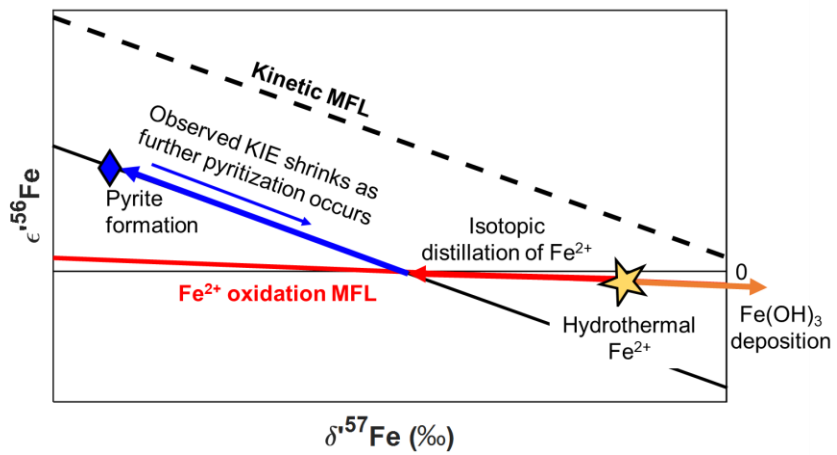
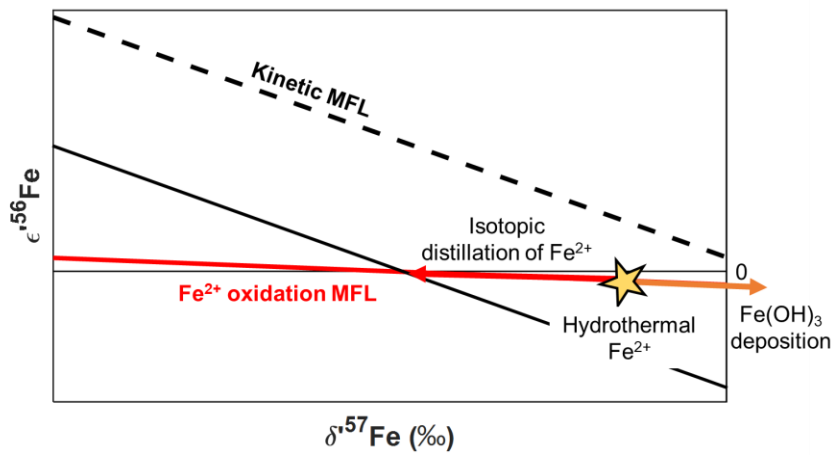
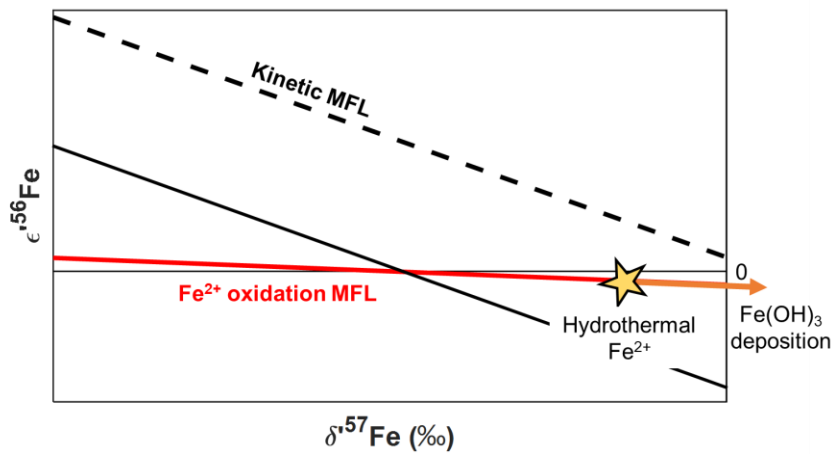


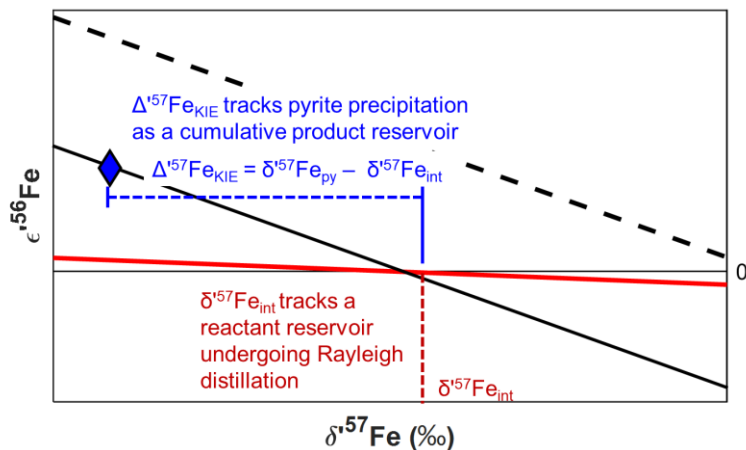
879

880 **Fig. S4.**

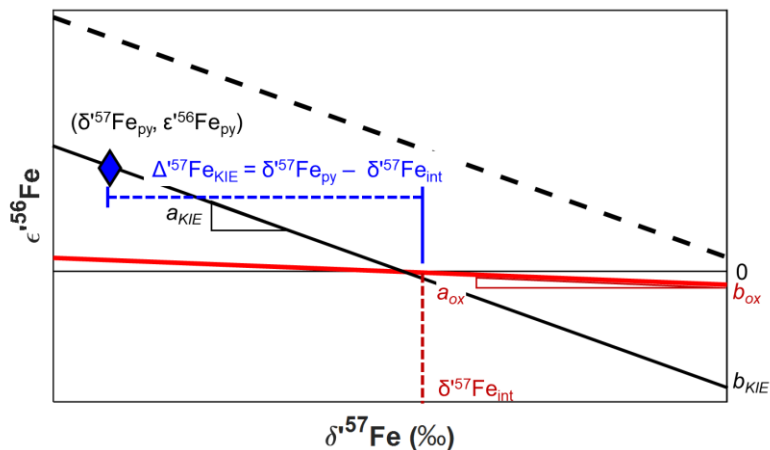
881 Distillation and mixing effects in triple Fe isotopic space. A: Comparison of effective MFL for
 882 Rayleigh distillation (dotted line) with the instantaneous MFL for the fractionation between
 883 reactant and product (solid line). The slopes equate to a difference in $\theta^{56/57}$ of just 0.0002, well
 884 within achievable analytical error for natural ranges of fractionation. B: Comparison of mixing
 885 curve (dotted line) between two arbitrary points (red circles) on the high-T equilibrium MFL
 886 (which is similar to our measured IF MFL), with the MFL itself (solid line). The maximum
 887 difference between the lines is 0.0069 in $\epsilon^{156}\text{Fe}$, much smaller than the achievable analytical error.
 888 Panels A and B indicate that distillation and mixing trends are identical to the instantaneous MFL
 889 of the process driving Fe isotopic fractionation over the naturally observed range of values, within
 890 analytical error on $\epsilon^{156}\text{Fe}$, which is typically on the order of ± 0.05 (95 % C.I.).

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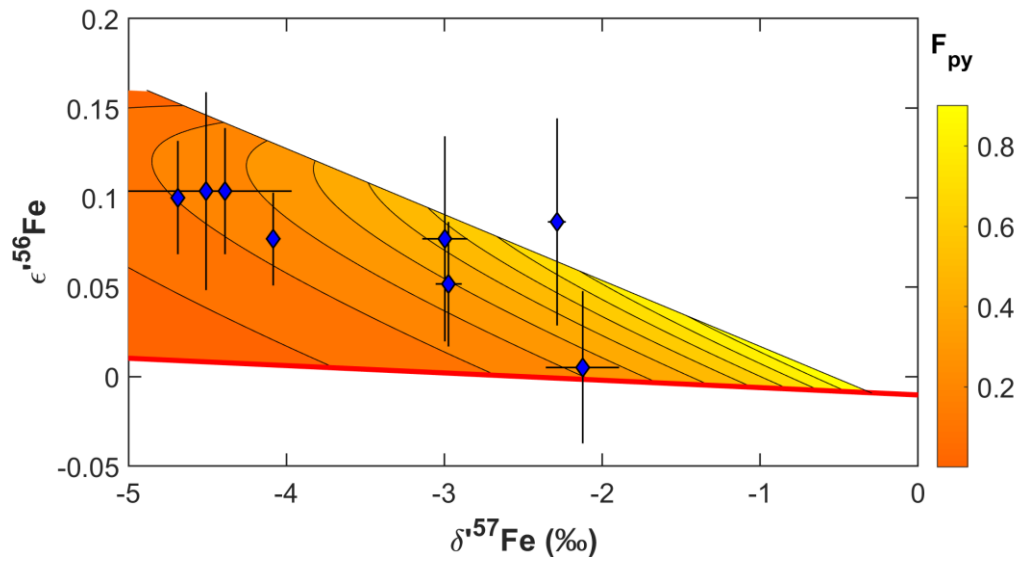


896

897 **Fig. S5.**

898 Conceptual illustration of the two step process (Fe^{2+} isotopic distillation by partial oxidation;
 899 subsequent partial pyritization) we propose for generating triple-Fe-isotopic composition of
 900 isotopically depleted pre-GOE pyrites, and the procedure for determining Fe isotopic
 901 contributions of pyritization, and initial isotopic composition of the pyrite-forming water mass,
 902 to the Fe isotopic composition of pyrite. The $\delta^{57}\text{Fe}$ value at where a trajectory for KIE during
 903 pyrite precipitation (with slope a_{KIE}) intercepts the oxidative IF MFL ($\delta^{57}\text{Fe}_{int}$) is determined by
 904 solving of simultaneous line equations. The difference between $\delta^{57}\text{Fe}_{int}$ and $\delta^{57}\text{Fe}_{py}$ gives the
 905 expression of the KIE during pyritization, which is used to determine the degree of pyritization
 906 (f_{py}) of the pre-pyritization water mass assuming that the pyrite is a cumulative product of all
 907 precipitated pyrite. $\delta^{57}\text{Fe}_{int}$ is assumed to be the $\delta^{57}\text{Fe}$ value of the pre-pyritization water mass,
 908 and its isotopic composition is assumed to reflect the degree of isotopically heavy Fe^{3+} -
 909 (oxyhydr)oxide removal (F_{ox}) that took place prior to the formation of pyrite.

910

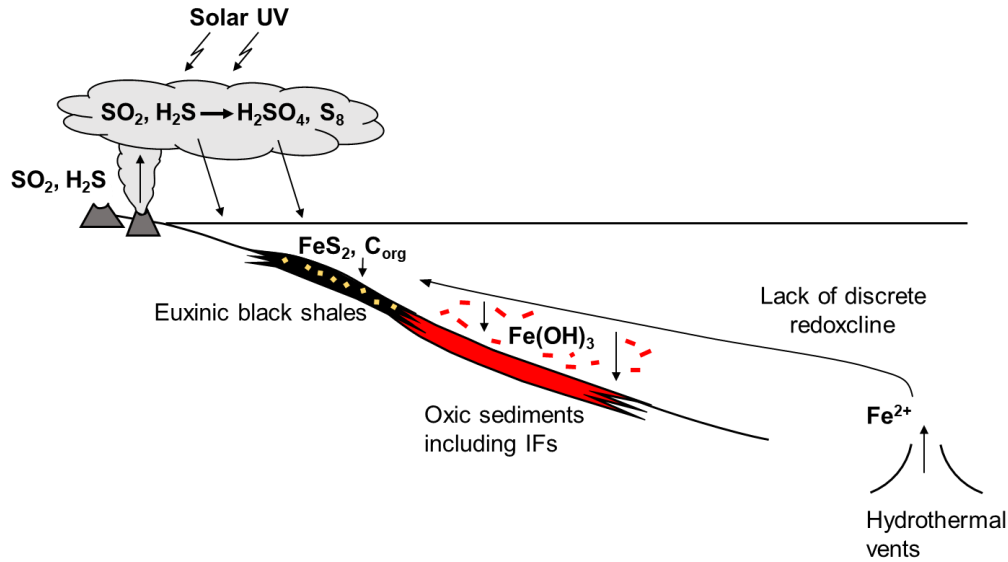


911

912 **Fig. S6.**

913 Determining the fractional pyrite sink for upwelled Fe (F_{py}) from triple-Fe-isotopic data. F_{py} values
 914 are calculated as $F_{py} = f_{py} \times (1 - F_{ox})$. Corresponding f_{py} and F_{ox} contours are plotted in Figure 2B
 915 of the main text.

916



917

918 **Fig. S7.**

919 Basin cross-section illustrating marine iron cycle before the GOE informed by triple-Fe-isotope
 920 systematics (9, 10, 27). Dissolved Fe^{2+} in deep-ocean waters fed by hydrothermal vents was
 921 upwelled onto continental margins. Oxidation of Fe^{2+} across a spatially diffuse redoxcline led to
 922 deposition of Fe^{3+} -(oxyhydr)oxide-rich sediments including IFs. In sedimentary environments
 923 with high organic carbon burial, the remaining dissolved Fe^{2+} was incorporated into pyrite, with
 924 pyritization before the GOE being limited by sulfur availability under a volcanically- and
 925 atmospherically-influenced sulfur cycle (3, 58).

926

Table S1										
Triple Fe isotope data for Archean-Paleoproterozoic pyrites, black shales, and IFs										
Sample	Age (Ga)	Sample type	$\delta^{56}\text{Fe}$	2 s.e	$\delta^{57}\text{Fe}$	2 s.e	$\epsilon^{56}\text{Fe}_{\text{exp}}$	$\epsilon^{56}\text{Fe}_{\text{eq}}$	2 s.e	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	-2.237	0.034	-3.296	0.044	-0.223	-0.026	0.058	22
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-014. The value of n refers to the number of standard-sample brackets analyzed.

Table S2									
Triple Fe isotopic data for pyrite precipitation experiments									
Sample	$\delta^{56}\text{Fe}-\delta^{56}\text{Fe}_0$	2 s.e.	$\delta^{57}\text{Fe}-\delta^{57}\text{Fe}_0$	2 s.e.	n(δ)	$\epsilon^{56}\text{Fe}_{\text{exp}}-\epsilon^{56}\text{Fe}_{\text{exp},0}$	$\epsilon^{56}\text{Fe}_{\text{eq}}-\epsilon^{56}\text{Fe}_{\text{eq},0}$	2 s.e.	n(ϵ)
SB1 FeS	0.243	0.064	0.381	0.091	5	0.049	0.027	0.044	21
SB1 Py	-2.201	0.064	-3.269	0.091	5	-0.070	0.126	0.045	26
SB2 FeS	0.159	0.064	0.276	0.091	5	-0.003	-0.020	0.077	10
SB2 Py	-2.582	0.064	-3.540	0.091	5	-0.092	0.120	0.058	9
SB3 FeS	0.232	0.064	0.326	0.091	5	0.009	-0.010	0.056	20
SB3 Py	-2.072	0.064	-3.080	0.091	5	-0.100	0.085	0.037	17
SB4 FeS	0.302	0.064	0.447	0.091	5	-0.007	-0.034	0.053	9
SB4 Py	-2.078	0.064	-3.077	0.091	5	-0.092	0.093	0.058	10
SB5 FeS	-0.026	0.061	0.133	0.115	5	0.001	-0.007	0.070	9
SB5 Py	0.091	0.061	-3.300	0.115	5	-0.046	0.152	0.025	27
SB6 FeS	-2.177	0.061	0.173	0.115	5	0.003	-0.007	0.057	9
SB6 Py	0.150	0.061	-3.083	0.115	5	-0.076	0.109	0.048	9
SB8 FeS	-2.039	0.061	0.361	0.115	5	0.019	-0.003	0.045	20
SB8 Py	0.289	0.061	-3.016	0.115	5	-0.026	0.155	0.027	28
SB9 FeS	-2.017	0.061	0.431	0.115	5	0.042	0.016	0.034	27
SB9 Py	0.301	0.061	-2.830	0.115	5	-0.063	0.107	0.062	20
SB10 FeS	-1.899	0.061	0.505	0.115	5	0.008	-0.022	0.038	29
SB10 Py	0.358	0.061	-2.906	0.115	5	-0.088	0.086	0.038	28

All isotope ratios are reported normalized to the composition of the starting material for experiments. The values of n(δ) and n(ϵ) refer to the number of standard-sample brackets analyzed for δ and ϵ measurements respectively. Starting material for SB 1-4, and SB 5-10, 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, 26)
FVG-1 765.8 BS	Jeerinah Fm	2.66	black shale	(9, 26)
FVG-1 774 BS	Jeerinah Fm	2.66	black shale	(9, 26)
FVG-1 827.8 BS	Jeerinah Fm	2.66	black shale	(9, 26)
REX 167.5	Hotazel Fm	2.43	IF	(2, 25, 45)
REX 187.5	Hotazel Fm	2.43	IF	(2, 25, 45)
Hotazel #41	Hotazel Fm	2.43	IF	(2, 25, 45)
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	(44, 46)

Reference numbers refer to Supplementary Reference List in the Supplementary Information

Table S4					
Estimated fractional size of iron sinks and shelf sedimentary Fe/S ratios for isotopically light pyrites					
Sample	F_{ox}	F_{py}	F_{sulf}	(Fe/S)_{sed}	Moles O₂ yield (per mole FeS₂)
EBA 2/30	0.38 ^{+0.45} _{-0.36}	0.68 ^{+0.30} _{-0.47}	0.48 ^{+0.14} _{-0.21}	0.9 ^{+2.0} _{-0.4}	2.3 ^{+0.2} _{-1.0}
DO29 14.95	0.22 ^{+0.51} _{-0.21}	0.60 ^{+0.32} _{-0.47}	0.65 ^{+0.12} _{-0.38}	0.7 ^{+1.2} _{-0.2}	2.4 ^{+0.1} _{-0.6}
WB-98 520.8	0.52 ^{+0.28} _{-0.44}	0.83 ^{+0.15} _{-0.26}	0.40 ^{+0.21} _{-0.20}	1.1 ^{+1.4} _{-0.5}	2.2 ^{+0.3} _{-0.7}
WB-98 519.68	0.64 ^{+0.24} _{-0.47}	0.98 ^{+0.02} _{-0.15}	0.36 ^{+0.34} _{-0.23}	1.4 ^{+2.6} _{-0.8}	2.1 ^{+0.3} _{-1.3}
SF-1 599.88	0.64 ^{+0.32} _{-0.46}	0.58 ^{+0.28} _{-0.41}	0.20 ^{+0.02} _{-0.08}	2.0 ^{+2.1} _{-1.0}	1.7 ^{+0.5} _{-1.0}
SF-1 623.6	0.50 ^{+0.31} _{-0.43}	0.58 ^{+0.29} _{-0.42}	0.30 ^{+0.03} _{-0.14}	1.3 ^{+1.7} _{-0.7}	2.1 ^{+0.3} _{-0.8}
FVG-1 752.8 A	0.57 ^{+0.32} _{-0.49}	0.54 ^{+0.37} _{-0.45}	0.23 ^{+0.02} _{-0.13}	1.7 ^{+3.4} _{-1.0}	1.9 ^{+0.5} _{-1.7}
FVG-1 752.8 B	0.52 ^{+0.30} _{-0.46}	0.54 ^{+0.30} _{-0.40}	0.25 ^{+0.02} _{-0.10}	1.5 ^{+1.6} _{-0.9}	2.0 ^{+0.4} _{-0.8}

Uncertainties are 95 % confidence intervals from Monte Carlo simulations. O₂ yields assume volcanic H₂S/SO₂ input ratio of 0. For volcanic H₂S/SO₂ input ratio of 1, O₂ yields are smaller by a factor of 2.5