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1 **Biological Regulation of Atmospheric Chemistry En Route to Planetary Oxygenation**

2 **Shortened Working Title:** Biogenic Haze Formation Fuels Planetary Oxidation

3 **Classification:** Physical Sciences: Earth, Atmospheric, and Planetary Sciences.

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24 **Contributions:** GI and AZ conceived the project. GI, AZ, MC and SP collected the samples. GI
25 and KW analyzed samples. MC developed the photochemical models and ran the simulations.
26 GI interpreted the data and wrote the manuscript with input from all co-authors. The authors
27 declare no competing financial interests.

28 **Key Words:** Sulfur Mass Independent Fractionation | Neoproterozoic | Organic Haze | Hydrogen
29 Loss | Planetary Oxidation

30 **ABSTRACT:** Emerging evidence suggests that atmospheric oxygen may have varied before
31 rising irreversibly ~2.4 billion-years-ago, at a time when primary atmospheric proxies indicate
32 reducing conditions. Significantly, however, temporal atmospheric aberrations towards more
33 reducing conditions—featuring a methane-derived organic-haze—have recently been
34 suggested, although their occurrence, causes and significance remain under-explored. To
35 examine the potential role for haze formation in Earth’s history, we targeted an episode of
36 inferred haze development. Our redox controlled (Fe-speciation) carbon- and sulfur-isotope
37 record reveals sustained systematic stratigraphic covariance, precluding alternate, non-
38 atmospheric, explanations. New photochemical models corroborate this inference, showing
39 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios are sensitive to the presence of haze. Utilizing existing age constraints, we
40 estimate that organic-haze developed rapidly, stabilizing within $\sim 0.3 \pm 0.1$ Myr, and persisted
41 for upwards of $\sim 1.4 \pm 0.4$ Myr. Given these temporal constraints and the elevated atmospheric
42 $p\text{CO}_2$ in the Archean, the sustained methane fluxes necessary for haze formation can only be
43 reconciled with a biological source. Correlative $\delta^{13}\text{C}$ and TOC measurements support the
44 interpretation that atmospheric haze was a transient response of the biosphere to increased
45 nutrient availability, with net methane fluxes controlled by the relative availability of organic-
46 carbon and sulfate. Elevated $p\text{CH}_4$ during haze episodes would have expedited planetary
47 hydrogen loss, with a single episode of haze development providing up to $2.6\text{--}18 \times 10^{18}$ moles
48 of O_2 equivalents to the Earth system. Our findings suggest the Neoproterozoic likely represented
49 a unique state of the Earth System where haze development played a pivotal, role in planetary
50 oxidation hastening the contingent biological innovations that followed.

51 **SIGNIFICANCE STATEMENT:** It has been proposed that enhanced methane fluxes to Earth’s
52 early atmosphere could have altered atmospheric chemistry, initiating a hydrocarbon-rich
53 haze reminiscent of Saturn’s moon, Titan. The occurrence, cause and significance of haze
54 development, however, remain unknown. Here, we test and refine the “haze hypothesis” by
55 combining an ultra-high-resolution sulfur- and carbon-isotope dataset with photochemical
56 simulations to reveal the structure and timing of haze development. These data suggest that
57 haze persisted for ~ 1 Myr, requiring a sustained biological driver. We propose that enhanced
58 atmospheric CH_4 , implied by the presence of haze, could have had a significant impact on the
59 escape of hydrogen from the atmosphere, effectively contributing to the terminal oxidation
60 of Earth’s surficial environments at ~ 2.4 Ga.

61 \body

62 **INTRODUCTION**

63 Quadruple sulfur isotope fractionation is one of the most robust geochemical tools available
64 to constrain the atmosphere's redox state, owing to intrinsic links between atmospheric
65 photochemistry and oxygen (1-11). Prior to ~2.4 Ga (5, 6), sedimentary S-phases display mass
66 independent S-isotope fractionation (S-MIF; $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S} \neq 0^1$), which is conspicuously absent
67 in the younger geological record (5-7, 11). The disappearance of S-MIF is widely cited as
68 reflecting a critical change in atmospheric state, where oxygen exceeded 0.001% of present
69 atmospheric levels (3) during the so-called Great Oxidation Event (GOE; 4, 5, 6, 12). More
70 recently, however, the perception of the GOE *sensu stricto* has been questioned by emerging
71 data derived from 3.0–2.5 Ga sediments, interpreted to represent both earlier
72 accumulation(s) of atmospheric oxygen/ozone (13-16), as well as transient descents toward a
73 reduced methane-rich atmospheric state (8, 9, 17, 18).

74 Interrogation of the temporal S-MIF record reveals additional details—variable magnitude
75 and changes in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope—which are suggested to reflect subtle atmospheric
76 compositional changes beyond the simple presence or absence of oxygen (6-10, 12, 17, 19-
77 21). Specifically, geochemical records from multiple continents reveal a broad correlation
78 between changes in the S-MIF record and highly ^{13}C -depleted organic carbon—termed C-S
79 anomalies (8)—which have been interpreted to reflect the periodic formation of a
80 hydrocarbon haze reminiscent to that observed on Saturn's moon Titan (8-10). While these
81 records have been used to paint an intriguing picture of Neoproterozoic atmospheric dynamics
82 in the prelude to the GOE (8, 9), a critical appraisal of the Neoproterozoic haze hypothesis awaits
83 (22). We present new, high-resolution, coupled quadruple sulfur- and carbon-isotope, Fe-
84 speciation, and TOC records (Figure 1) from the youngest of the three C-S anomalies identified
85 in core GKF01, obtained from Griqualand West Basin, South Africa (SI Appendix, Figure 1A; SI
86 Appendix; 9, 15, 23, 24), resulting in the highest temporal-resolution stratigraphic study yet
87 conducted in the Archean. Critical to testing the haze hypothesis, our geochemical records
88 reveal the timing and structure of a C-S anomaly, which when combined with an updated
89 photochemical model, demonstrate a connection between changes in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope and

¹ Sulfur-isotope ratios are conventionally reported in delta (δ) notation, and reflect the permil (‰) deviation of the ratio of the least abundant ($^{33,34,36}\text{S}$) to the most isotope (^{32}S) relative to the same ratio in an international reference standard (Vienna Canyon Diablo Troilite, V-CDT). For example, $\delta^{34}\text{S} = ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{V-CDT}}) - 1$. The majority of processes fractionate S-isotopes mass dependently, whereby $\delta^{33}\text{S} \approx 0.515 * \delta^{34}\text{S}$ and $\delta^{36}\text{S} \approx 1.91 * \delta^{34}\text{S}$. Departure from mass-dependent behavior, or mass-independent fractionation (MIF), is expressed in capital-delta (Δ) notation as either non-zero $\Delta^{33}\text{S} [(^{33}\text{S}/^{32}\text{S})_{\text{sample}} / (^{33}\text{S}/^{32}\text{S})_{\text{V-CDT}} - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{V-CDT}})^{0.515}]$ or $\Delta^{36}\text{S} [(^{36}\text{S}/^{32}\text{S})_{\text{sample}} / (^{36}\text{S}/^{32}\text{S})_{\text{V-CDT}} - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{V-CDT}})^{1.9}]$.

90 atmospheric haze. Following this, we speculate on the wider role of episodic haze formation
91 in planetary oxidation.

92 RESULTS

93 In core GKF01, the upper Nauga Formation reveals large multiple S-isotope variability, with
94 non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Figures 1–2, SI Appendix, Fig. S2) reflecting photochemical production
95 in an atmosphere devoid of significant oxygen (1-3, 6, 7). The majority of these data form a
96 linear $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ array (Figure 2), typifying core GKF01 (9, 18) and the wider Neoproterozoic as a
97 whole ($\Delta^{36}\text{S} \approx -0.9 \times \Delta^{33}\text{S}$). Of importance for this study, the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ record reveals a coherent
98 stratigraphic structure, with a remarkably stable background ($\Delta^{36}\text{S}/\Delta^{33}\text{S} = -0.9$) punctuated by
99 a spectacular negative excursion between 840.0 and 827.87 m core depth. During the
100 excursion $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios become increasingly negative (Figure 1B), attaining a steeper slope
101 of ~ -1.5 , before relaxing back towards the background $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ (-0.9 ; Figures 1–2). While the
102 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ data displays little variability outside of the identified excursion (Figure 2), the
103 magnitude of the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ is highly variable, carrying positive and negative arithmetic
104 signs, respectively (SI Appendix, Fig. S2). Consequently, it appears that the dominant sulfur
105 source for pyrite formation over the examined interval was elemental sulfur, inferred to carry
106 a positive $\Delta^{33}\text{S}$ (7, 18, 25). Atypically, the $\delta^{34}\text{S}$ record displays little variability, with the
107 exception of two relatively more ^{34}S depleted samples seen at ~ 840 m (Figure 1).

108 Moving in phase, or perhaps even leading the S-isotope record, $\delta^{13}\text{C}_{\text{Org}}$ is also observed to
109 descend to extremely low values (less than -37 ‰; Figure 1b); a relationship that is particularly
110 apparent in Figure 3a where $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ less than -1 corresponds to $\delta^{13}\text{C}_{\text{Org}}$ ² less than -37 ‰,
111 and the most ^{13}C -depleted samples relate to the lowest $\Delta^{36}\text{S}/\Delta^{33}\text{S}$. We observe additional low
112 $\delta^{13}\text{C}_{\text{Org}}$ values (~ -35 ‰) below the C-S anomaly that are not associated with changes in
113 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$, but correspond to small-scale increases in TOC typical of the intercalated
114 mudstones that are below the scale to be represented in Figure 1.

115 The C-S anomaly is not confined wholly to the mudstone interval, as cursory consideration of
116 Figure 1 would suggest. The decreases in both geochemical parameters are observed to have
117 occurred by 840 m core depth; however, close inspection of detailed core logs/photos (SI
118 Appendix, Fig. S3) shows that a lithological change from carbonate to mudstone occurs 0.6–
119 1.0 m above this horizon. Similarly, while the most depleted $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios are confined to
120 the basal-half of the mudstone, the return to background $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ is not established until

² Carbon-isotope data are expressed as permil deviations from the Vienna-PeeDee Belemnite (V-PDB) standard: $\delta^{13}\text{C}_{\text{Org}} = ((^{13}\text{C}/^{12}\text{C}_{\text{Sample}})/(^{13}\text{C}/^{12}\text{C}_{\text{V-PDB}})) - 1$.

121 827.8 m, some 1.5m above the reestablishment of calcareous sedimentation (Figures 1; SI
122 Appendix, Fig. S3). These observations require chemostratigraphic controls beyond simple
123 facies or lithological changes.

124 DISCUSSION

125 THE CAUSES AND SIGNIFICANCE OF THE SULFUR AND CARBON ISOTOPE COVARIATION

126 The broad correspondence between low $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ and $\delta^{13}\text{C}_{\text{Org}}$ has formed the cornerstone of
127 the “haze hypothesis”, whereby enhanced methane flux (manifested as low $\delta^{13}\text{C}_{\text{Org}}$) is
128 hypothesized to have promoted organic-haze formation and altered atmospheric chemistry
129 (registered as $\Delta^{36}\text{S}/\Delta^{33}\text{S}$; 8, 9). The low-resolution records generated in these prior studies,
130 however, have precluded rigorous examination of this hypothesized link, which in turn has
131 obfuscated the wider role of haze formation within the evolution of the ancient Earth system.
132 As a result this early work failed to reveal the stratigraphic structure of a C-S anomaly beyond
133 a few scattered data points. Our geochemical records (Figures 1; SI Appendix, Fig. S2) provide
134 a framework from which to examine the origin of the observed C- and S-isotope covariation.

135 The $\delta^{13}\text{C}$ of sedimentary organic matter is an integrated product, combining varying
136 contributions from different biological sources. Contemporary and Phanerozoic $\delta^{13}\text{C}_{\text{Org}}$
137 records display restricted variability owing to the limited C-isotope fractionation associated
138 with heterotopic respiration. The Neoproterozoic, by contrast, features a more pronounced
139 range of $\delta^{13}\text{C}_{\text{Org}}$, indicating more pervasive incorporation of ^{13}C -depleted substrates,
140 particularly methane (26). Accordingly, the low $\delta^{13}\text{C}_{\text{Org}}$ ($< -37\text{‰}$) seen in the C-S anomaly, and
141 probably the intermediate $\delta^{13}\text{C}_{\text{Org}}$ ($< -35\text{‰}$) in the basal part of the examined succession ($<$
142 840 m; Figure 1), speak to substantial methane incorporation into sedimentary organic
143 matter. In greater detail, this incorporation involves the interplay between localized methane
144 production (methanogenesis), oxidation and assimilation (methanotrophy; 26). Therefore,
145 the low $\delta^{13}\text{C}_{\text{Org}}$ data observed in GKF01 (and other Neoproterozoic sedimentary successions) can
146 be explained in two ways: (i) increased methanotrophy assimilating more methane into the
147 sedimentary record independent of the methane flux (26, 27) or (ii) enhanced
148 methanogenesis, increasing environmental methane availability, with a parallel increase in
149 methanotrophy (8, 9). Sedimentary $\delta^{13}\text{C}_{\text{Org}}$ values are controlled *locally*, and reflect the carbon
150 utilization strategies of the microbial communities from which the organic matter is sourced.
151 Therefore, the haze hypothesis does not require every inflection in the $\delta^{13}\text{C}_{\text{Org}}$ record to
152 correspond to altered atmospheric chemistry. In fact, one prediction of the haze hypothesis
153 is that there should be instances where $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ and $\delta^{13}\text{C}_{\text{Org}}$ are decoupled (8), such as below
154 840 m in core GKF01 (Figure 1).

155 **AN ALTERNATE, NON-ATMOSPHERIC, CONTROL ON $\Delta^{36}\text{S}/\Delta^{33}\text{S}$?**

156 The haze hypothesis is reliant on the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ parameter faithfully recording what is inferred
157 to be regional to global-scale atmospheric chemistry. The high-resolution dataset we present
158 here (Figure 1) provides the perfect opportunity to test alternative hypotheses, whereby non-
159 atmospheric, sediment-hosted, processes could produce the observed changes in the
160 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ record.

161 Biological metabolic processes are known to impart small mass-dependent effects during
162 inter- and intra-cellular (un)mixing processes (19, 28). Biologically mediated mass
163 conservation effects are known to preferentially effect $\Delta^{36}\text{S}$, resulting in distinctive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$
164 slopes (~ 7 ; 28), potentially overprinting the atmospheric $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ signal. The extent of such
165 a biological overprint is quasi-predictably governed by initial source of pyrite-sulfur, producing
166 a scalene mixing-field in $\Delta^{36}\text{S}-\Delta^{33}\text{S}$ quadruple-isotope space (Figure 2B; 29). Since microbial
167 sulfate reduction (MSR) imparts the largest biological S-isotope fractionations, this biological
168 effect is most pronounced when the pyrite-sulfur is dominated by a sulfate precursor
169 (negative $\Delta^{33}\text{S}$) and becomes progressively more muted when elemental sulfur (positive $\Delta^{33}\text{S}$)
170 dominates the pyrite-sulfur pool (29). Examination of Figures 2 and Fig. S2 (SI Appendix)
171 reveals the pyrite throughout the studied interval carries a pronounced and exclusively
172 positive $\Delta^{33}\text{S}$, in-turn implying an elemental sulfur source, which is expected to be less
173 susceptible to modification by MSR (Figure 2). In addition to altering $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, microbial
174 processes are also generally associated with pronounced changes in $\delta^{34}\text{S}$ (60–70‰; 30).
175 However, as described above, the $\delta^{34}\text{S}$ record in the succession we examined is remarkably
176 stable (Figures 1, 3C), offering little support for a biologically mediated model (19).

177 Thermochemical sulfate reduction (TSR) can also impart a distinctive S-MIF signature (Figure
178 2B); however, this process also cannot explain our S-isotope observations. Firstly, we see no
179 evidence for selective hydrothermal activity associated with TSR in strata between 840.0 and
180 827.87 m. Decisively, TSR has been shown experimentally to impart large $\Delta^{33}\text{S}$ enrichments
181 without significant changes in $\Delta^{36}\text{S}$ (31). Addition of TSR-derived sulfur, therefore, would serve
182 to increase $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios, which is contrary to what we observe (Figure 2).

183 A final possibility invokes an additional, and isotopically distinct, S-MIF production pathway
184 capable of producing an additional sulfur pool with a distinct and different $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ (< -1.5),
185 which could selectively contribute to pyrite genesis under variable conditions (32). The
186 observed change in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ could, therefore, reflect electron donor availability, highlighting
187 a potential localized control on the degree of pyritization, whereby high TOC permitted
188 selective access to a recalcitrant sulfur pool. Following this scenario, the increased TOC

189 observed in the C-S anomaly (Figure 1), could potentially provide a sediment-hosted
190 explanation for the observed coupled C- and S-isotope covariation. This explanation would
191 require a ubiquitous association between low $\Delta^{36}\text{S}/\Delta^{33}\text{S}$, $\delta^{13}\text{C}_{\text{Org}}$ and high TOC, which is not
192 observed in our data or in previous datasets (Figures 1–3; 8, 9, 22). For example, closer
193 examination of Figure 3B shows there are samples that are enriched in TOC (~ 1 Wt. %) yet
194 display typical $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios (-0.9). Similar trends are also obvious in published records, with
195 typical $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios being frequently observed in tandem with high TOC abundances (5 %
196 Wt. %; 9). Also, if sedimentary $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios were truly independent of time-dependent
197 changes in atmospheric chemistry, the necessary refractory sulfur pool should be ever-
198 present (independent of lithology) and should be observed in other portions of the geological
199 record. For instance, a secondary sedimentary sulfur pool might be expected to be
200 intermittently incorporated into pyrite under a particular range of depositional conditions,
201 producing highly variable $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values. This is not the case here (Figure 1), and is also at
202 odds with the wider Archean $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ record (19). Moreover, SIMS analyses reveal that
203 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ trends are conserved at the grain scale between different populations of pyrite
204 within the GKF01 core as a whole (18). Therefore, any model driven by electron donor
205 availability, reliant on a “ghost sulfur pool”, cannot be responsible for the observed change in
206 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ revealed in the C-S anomaly (Figure 1). Taken together, sediment-hosted processes,
207 such as biological modification, thermochemical alteration and differential pyrite genesis, fail
208 to satisfactorily explain the systematic changes in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ starting at 840 m, leaving an
209 atmospheric origin as the most parsimonious explanation of these data.

210 **PHOTOCHEMICAL MODELING OF $\Delta^{36}\text{S}/\Delta^{33}\text{S}$**

211 Assimilating the arguments above, the two isotopic systems (C and S) that form the keystone
212 of the haze hypothesis are sensitive to perturbations on different spatial, and potentially
213 temporal, scales. In principle, low $\delta^{13}\text{C}_{\text{Org}}$, and hence methane production/consumption,
214 should be ubiquitous in the Archean, responding to local-scale changes in organic matter
215 quality and quantity (8, 9, 26). In an atmospheric sense, however, it is unlikely that a short-
216 lived change akin to what we observed in the intercalated subordinate mudstones in the basal
217 part of the succession (> 840 m depth; Figure 1) would result in a change in atmospheric
218 methane concentrations capable of instigating haze formation. Instead, it would require a
219 sustained regional increase in methane fluxes, caused by changes in nutrient delivery or
220 redistribution in the oceans (discussed below), to plausibly increase atmospheric $p\text{CH}_4$
221 sufficiently to instigate haze formation. If haze development was substantial enough to

222 enshroud the planet, it is also possible that $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ could be decoupled from $\delta^{13}\text{C}_{\text{Org}}$, if the
223 site of methane production/consumption was occurring elsewhere.

224 To examine the direct link between $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values and atmospheric chemistry, we updated
225 an Archean 1-D photochemical model (7) to predict $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$, and trace $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios
226 through an atmospheric reaction network. Details of the model and our preliminary validation
227 approach are provided in the [SI Appendix](#). The most significant changes from the initial
228 predictions of Claire et al. (7) arise from the inclusion of new data allowing $\Delta^{36}\text{S}$ predictions,
229 and the use of newly measured SO_2 photodissociation cross-sections (33). As noted previously
230 (7, 34), the earlier SO_2 cross-sections (35) produced results at odds to the commonly accepted
231 interpretation of the geologic record: predicting positive $\Delta^{33}\text{S}$ in sulfate and negative $\Delta^{33}\text{S}$ in
232 elemental sulfur. Incorporating the revised cross-sections (33) resolve this data-model
233 mismatch, and now predict exit channels with the arithmetic sign commonly seen in the rock
234 record ([Figures 4–5](#)). However, it is important to note our model still fails to reproduce both
235 the magnitude of the S-MIF and the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio archived in the geological record ([Figures](#)
236 [1, 4–5](#); [S SI Appendix](#)). A detailed exploration of this discrepancy exceeds the scope of this
237 study, but likely reflects uncertainties concerning the primary S-MIF generating mechanism(s)
238 included within the model and/or the composition of the Archean background state ([Figure](#)
239 [4](#); 7). Both of these potential sources of uncertainty are the focus of on-going research and
240 remain fundamental to successful inverse reconstruction of the Archean atmosphere.

241 [Figure 4A](#) provides insight into the transmittance of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios through an atmospheric
242 reaction network. Exploiting the putative Neoproterozoic atmospheric composition (the
243 “standard model”) envisaged by Claire et al (7), sulfur-species leave the atmosphere unequally
244 divided between three exit channels. The model predicts that aerosol exit channels (SO_4 and
245 S_8) feature fairly homogeneous $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ signatures irrespective of the height of their
246 tropospheric genesis. By contrast, the predicted $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios communicated to SO_2 vary
247 substantially through the troposphere. SO_2 exits the atmosphere primarily dissolved in
248 rainwater, so homogenization likely precludes the expression of the modeled $\Delta^{36}\text{S}/\Delta^{33}\text{S}$
249 variability ([Figures 4–5](#)). Aerosol species, by contrast, should serve as more instantaneous
250 vectors carrying the entire range of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ to the Earth’s surface, resulting in spatial
251 variability independent of atmospheric chemistry. Consequently, the modeled $\Delta^{36}\text{S}/\Delta^{33}\text{S}$
252 stability in aerosols is reassuring, advocating $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios as a conservative parameter
253 reflective of a given atmospheric state; that, unlike the absolute S-MIF magnitude (32), would
254 be unlikely to display significant widespread spatial variability under a truly global
255 atmospheric state. This fits well with the stable background $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ (-0.9) that is observed

256 throughout the majority of the 100 m (11.7 ± 3.3 Myr; [SI Appendix](#)) of examined core ([Figure](#)
257 [1](#)), and the wider Archean record (19).

258 The utility of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios is extended via examination of [Figure 4B](#). Here, we present
259 results from 22 distinct model atmospheres where the total volcanic sulfur flux was varied
260 over two orders of magnitude. This experiment alters the atmospheric redox state, enhancing
261 the relative importance of the S_8 exit-channel in the more sulfur-laden atmospheres. [Figure](#)
262 [4B](#) shows that within each model atmosphere the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios of all exit-channels remain
263 homogenous (± 0.1), in-turn supporting our claim that $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ reflects the instantaneous
264 state of atmospheric chemistry. The range and systematic decrease in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ observed
265 between simulations (+0.2 to -0.4) highlights the sensitivity of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios to atmospheric
266 composition, advocating $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ as a promising atmospheric probe—A conclusion that
267 extends beyond both the chosen experiment (sulfur loading) and our predicted magnitudes.

268 To examine the ability of an organic haze to modulate $\Delta^{36}\text{S}/\Delta^{33}\text{S}$, we varied the O_2 and CH_4
269 fluxes (7, 10) to create two different hazy states, ([Models 1 & 3 in Figure 5B & 5D](#)) along with
270 an additional clear-skies atmospheric state ([Model 2 in Figure 5C](#)). Similar to the cases
271 presented previously ([Figure 4A](#)), the incorporation of the new cross-sections (33) causes the
272 $\Delta^{33}\text{S}$ predictions to deviate from those presented previously (7), qualitatively approximating
273 the geological record. Our simulated hazy atmospheric states produce $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slopes (+0.19,
274 [Figure 5B](#) and -0.52, [Figure 5D](#)), which differ from the clear-skies simulation (-0.04, [Figure 5C](#)).
275 The clear-skies simulation in [Figure 5C](#) has distinct, but broadly similar, boundary conditions
276 to the “standard atmosphere” ([Figure 4A](#); 7) so their similar $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ provides additional
277 confidence that $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slopes are the product of specific atmospheric states, and do not
278 vary widely with minor fluctuations in atmospheric state. We stress again that the absolute
279 values of these predictions are preliminary and will likely change with additional model
280 complexity ([SI Appendix](#)). Our approach here is not sufficient to make the claim that haze is
281 uniquely responsible for variations in the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope from -0.9 to -1.5. Rather, our more
282 simple aim is to test the assertion that atmospheric reaction rates, exit channels and UV
283 transparency vary sufficiently underneath a hazy atmosphere to modulate the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios
284 (7-10). The predicted uniformity of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios, expressed in all atmospheric exit
285 channels, ultimately facilitates transmission from the atmosphere where they may be
286 preserved in the geological record (8, 9, 18)—a key prediction of the haze hypothesis.
287 Furthermore, the different $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios produced under different atmospheric hazy
288 regimes provides support to the idea that hazes in different parts of Earth history (e.g., before

289 and after substantial biospheric O₂ fluxes) might yield unique S-MIF signatures (cf. [Figures 5B](#)
290 [and 5D](#); 8).

291 A caveat to these inferences hinges on pyrite genesis, the global vs. regional extent of the
292 haze, and the photochemical origin of the pyrite-sulfur precursor. Under a global hazy
293 atmospheric configuration, after mixing into the seawater sulfate reservoir, putative hazy-
294 type $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios (-1.5) would be preserved within pyrite independent of its initial sulfur
295 source (e.g., sulfate or elemental sulfur; [Figures 4 & 5](#)). If regional haze development were
296 possible, then conceivably pyrite could have inherited either a typical Archean $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ (-0.9)
297 or a steeper hazy-type $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ (-1.5). Here, elemental sulfur would have carried the
298 atmospheric $\Delta^{36}\text{S}/\Delta^{33}\text{S}$, and thus the localized instantaneous chemical state directly to pyrite.
299 Contrastingly, pyrite produced from seawater sulfate would be expected to preserve a
300 globally integrated signal, facilitated via oceanic mixing. Therefore, sulfate-sourced pyrite
301 could carry a slope more characteristic of haze beneath a localized clear-skies atmospheric
302 regime. Unfortunately, the current dataset displays exclusively positive $\Delta^{33}\text{S}$ ([Figures 2](#), [SI](#)
303 [Appendix, Fig. S2](#)), thus precluding a definitive appraisal of the precursor sulfur (18) in this
304 particular C-S anomaly. Given that our pyrite record is derived from predominantly sulfur
305 aerosols, reflecting instantaneous atmospheric chemistry, the shift in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ indicates core
306 GKF01 was deposited beneath a hazy-sky, consistent with the observed C- and S-isotope
307 covariation ([Figures 1 & 3A](#)).

308 **CONSTRAINING THE TIMING AND DRIVERS OF ATMOSPHERIC HAZE FORMATION**

309 These geochemical and computational arguments lend credence to the haze hypothesis.
310 Accordingly, we interpret the C-S anomaly as a chemostratigraphic marker of atmospheric
311 haze development. The well-defined structure of the high-resolution C-S anomaly ([Figure 1](#))
312 allows us to extract time constraints to reveal the tempo and duration of an inferred episode
313 of haze development. Utilizing existing radiometric age constants (36-40; [SI Appendix](#)), and
314 assuming linearity, application of average sedimentation rates ([SI Appendix](#)) suggest that haze
315 persisted for 1.4 ± 0.4 Myr, attaining maximum haze thickness (lowest $\Delta^{36}\text{S}/\Delta^{33}\text{S}$) over $0.3 \pm$
316 0.1 Myr (3 m). Adopting these temporal constraints, even acknowledging the potential
317 uncertainties of our approach (see [SI Appendix](#) for derivation and uncertainties), the
318 development of Neoproterozoic atmospheric haze is inconsistent with rapid release of methane
319 from a standing methane reservoir (such as methane hydrates), and requires a more sustained
320 methane flux to the atmosphere.

321 While contemporary sedimentary methane production is substantial, little escapes to the
322 ocean-atmosphere system owing to efficient consumption by either aerobic methanotrophs,

323 or by a consortium of anaerobic methanotrophs and sulfate reducers (AOM) at the sulfate-
324 methane transition zone (41-43). Nevertheless, within the oxygen- and sulfate-starved
325 Neoproterozoic oceans (44-46) methanogens would have proliferated, whilst methanotrophs and
326 AOM would have been spatially restricted. Correspondingly, enhanced Neoproterozoic
327 methanogenesis would have likely translated into elevated atmospheric CH₄ fluxes (41-43),
328 supporting large background Archean CH₄ concentrations (7, 10, 20, 21, 41, 47). When the
329 CH₄:CO₂ mixing ratio exceeded a critical threshold of ~ 0.1, this CH₄ flux would have formed
330 an organic-rich hydrocarbon haze (9, 10, 20, 47), although the regional/global extent of these
331 haze(s) require further study.

332 Methanogens feature a complex biochemistry dependent on nickel-based metallo-enzymes
333 (48), which they use to produce methane at the expense of simple carbon compounds and
334 molecular hydrogen (49, 50). Although reconstructed marine nickel concentrations suggest
335 that post-2.7 Ga oceans were nickel limited (49, 50), it is improbable that nickel *alone* was a
336 stimulus for episodically heightened methane production necessary for haze production.
337 Neoproterozoic oceanic nickel depletion has been attributed to long-term unidirectional mantle
338 cooling, changing the chemical composition of igneous rocks and concomitant marine nickel
339 delivery (49, 50). In contrast, haze formation was geologically rapid, and occurred repeatedly
340 in the prelude to the GOE (8, 9), thus requiring a recurrent, yet geologically short-lived, driver.
341 While it is feasible that episodic volcanism could supply reactive igneous rocks, secular mantle
342 cooling should have ensured their nickel content was progressively lower (49, 50). Perhaps
343 more importantly, it is difficult to envisage a *solely* volcanic/hydrothermal driver that
344 effectively decouples nickel delivery from other bio-essential elements (e.g., P, N, Fe, Mo et
345 cetera; 13).

346 Alternatively, episodic top-down stimulation of the entire biosphere, via enhanced primary
347 productivity in the surface waters, could provide a more satisfactory trigger for haze
348 development. This inference is supported by relatively high total organic-carbon (TOC)
349 abundances ($\geq 2\%$) within the C-S anomaly (Figure 3B) compared to the Neoproterozoic average
350 (1.5 ± 1.3 Wt. %; 51). Although high TOC abundances could reflect either diminished dilution
351 by carbonate, enhanced productivity or preservation, the consistently low Fe_{HR}/Fe_T (< 0.38)
352 ratios observed during the C-S anomaly (Figure 1B), suggest that oxic sedimentation persisted³

³ Summation of the oxic (Fe_{carb}, Fe_{ox} and Fe_{mag}) and anoxic Fe extractions (Fe_{py}) defines the highly reactive Fe pool (Fe_{HR} = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}), which when normalized to the total Fe pool (Fe_T) and Fe_{py} permits distinction between oxic (Fe_{HR}/Fe_T = < 0.22), ferruginous (Fe_{HR}/Fe_T = > 0.38 and Fe_{py}/Fe_{HR} = < 0.7) and euxinic Fe_{HR}/Fe_T = > 0.38 and Fe_{py}/Fe_{HR} = > 0.8) depositional conditions. Details of mineral phases that comprise these operationally defined

353 (9, 15), arguing against a preservational control. Contrasting redox inferences gleaned from
354 the S-MIF and the Fe-speciation records further implicate marine productivity with
355 atmospheric haze development. Here the low Fe_{HR}/Fe_T (< 0.38) ratios, in concert with limited
356 enrichments in redox sensitive trace metals (e.g. Mo, Re and U; 15), signal mildly oxic
357 sedimentation against an anoxic atmospheric backdrop (Figure 1b). Given that atmospheric
358 models insinuate O_2 residence times on the order of a few hours (7) and extremely reducing
359 tropospheric conditions, these data can only be reconciled by oxygenic photosynthesis (15)
360 creating locally oxygenated water column conditions and the development of an oxygen oasis
361 (52). The production of oxygen and organic matter in surface environments and their
362 destruction in deeper waters, the sediment–water interface and below, had the potential to
363 spatially decouple oxygen and methane production; thereby, offering a mechanism where
364 methane could have escaped water column reoxidation and contributed to the atmospheric
365 methane burden.

366 Excluding a facies control on the observed TOC increase is more difficult. The deepening
367 experienced during the mudstone deposition probably inhibited carbonate deposition via
368 isolation from the photic zone (23), hence reducing the dilutive effects of the biogenic
369 carbonates during the C-S anomaly. That said, the small-intercalated mudstones in the basal
370 part of the examined section (< 840 m) represent the same facies change, yet do not display
371 the isotopic covariation that defines the C-S anomaly. This difference we explain as a function
372 of scale: The mudstone containing the C-S anomaly has known lateral facies equivalents in
373 core GKP01 (15, 23, 53), so independent of dilution-type effects, TOC-rich sediments were
374 deposited across a larger area of the Griqualand West basin during the C-S anomaly. Thus
375 increased TOC deposition could have supplied ample organic carbon to fuel regionally
376 pervasive methanogenesis, potentially enhancing methane fluxes to the atmosphere.
377 Importantly, consistent with the predictions of atmospheric simulations (7), the persistence
378 of large magnitude S-MIF with changing $\Delta^{36}S/\Delta^{33}S$ (Figure 2; SI Appendix, Fig. S1)
379 demonstrates that the atmosphere remained essentially oxygen free (1-3, 6, 7, 10) despite
380 evidence for enhanced oxygen production (9, 15). Apparently the global sinks of water column
381 reductants (e.g. Fe^{2+} ; 4), combined with reduced atmospheric gases (e.g., H_2 , CH_4), were still
382 sufficient to prevent atmospheric oxygenation at this time (7, 10).

383 Deciphering the ultimate stimulus for the inferred biospheric invigoration, and associated
384 ecological shifts, remains difficult, yet given the persistence of large magnitude S-MIF (Figures

Fe pools and the empirically threshold values that separate each redox regime are given in the SI Appendix.

385 1–2, SI Appendix, Fig. S2), there is no need to invoke planetary scale oxidative weathering by
386 free atmospheric O₂ (13, 14). Alternate mechanisms such as episodic chemical weathering
387 driven by changes in climate and/or tectonics could directly, or indirectly (via changes in ocean
388 circulation and upwelling efficiency), have delivered the necessary nutrients to the photic
389 zone over widespread areas. Additionally, the emergence and proliferation of terrestrial life
390 (51) should have also revolutionized weathering efficiency via ground level oxidative
391 weathering (54), providing another mechanism to flux nutrients (e.g., P and bio-essential trace
392 elements), along with sulfate to the ocean, without any significant leak of O₂ to the
393 atmosphere.

394 Pyrite δ³⁴S values are lowest at the base of the C-S anomaly (~ -15 ‰) before stabilizing to
395 values close to those reconstructed from contemporaneous carbonate-associated sulfate
396 from the Campbellrand carbonate platform (Figures 1, 3C; 55;). While these few ³⁴S depleted
397 samples could easily reflect changes in sediment-housed microbial sulfur cycling and
398 associated pyrite formation (19, 56), these data can also be reconciled with an initial
399 weathering pulse delivering sulfate, and presumably other nutrients, to the biosphere.
400 Beyond the fortuitous placement of the low δ³⁴S at the base of the C-S anomaly within an
401 otherwise stable δ³⁴S record (Figures 1, 3C), unequivocal discrimination between these two
402 potential explanations of the δ³⁴S data is challenging on the basis of bulk SF₆ measurements
403 alone. Enigmatically, however, radiogenic ¹⁸⁷Os/¹⁸⁸Os_i ratios have recently been reported from
404 the Mt. McRae shale, which can only be reconciled with crustal ¹⁸⁷Os ingrowth via β⁻decay of
405 ¹⁸⁷Re, followed by remobilization and delivery to the marine reservoir (14). The Mt. McRae
406 succession is perhaps one of the most celebrated Archean sedimentary successions,
407 containing the ~2.5 Ga trace-element enrichments that were interpreted to represent pre-
408 GOE whiffs of oxygen (13). Interestingly, as noted by Zerkle et al. (9), the upper Mt. McRae
409 shale also features a change in Δ³⁶S/Δ³³S to lower values (57), which is broadly associated with
410 a change in δ¹³C_{Org}—exhibiting some interesting parallels with the data presented herein.
411 Unfortunately the Mt. McRae shale data are of insufficient resolution to make meaningful
412 comparisons with our own, and no Re-Os data exist for the C-S anomaly examined in Figure 1.
413 Clearly further targeted SF₆ and SIMS analysis, coupled with the application of sensitive
414 radiogenic isotope tracers (e.g. Re-Os; 58), to this and other C-S anomalies (8, 9), has the
415 potential to elucidate the source of the nutrients (weathering vs. oceanic nutrient
416 redistribution) and should be a fruitful avenue of future research.

417 From an Earth system perspective, low seawater sulfate concentrations were likely an
418 important prerequisite for haze formation, allowing methane to escape AOM in the sediment

419 pile and enter the atmosphere. The Neoproterozoic oceans as a whole are inferred to have had
420 historically low sulfate concentrations (16, 45), poisoning the biosphere at a tipping point,
421 allowing the balance between methane production and consumption to shift rapidly following
422 pulses of marine fertilization and attendant sedimentary carbon delivery (8). Consequently,
423 enhanced productivity would be expected to strengthen methane production, creating
424 inflections in the $\delta^{13}\text{C}$ isotope record that are only coupled with changes in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ when
425 methane fluxes are sufficient to affect atmospheric chemistry. Eventually, however, enhanced
426 terrestrial colonization (51, 54), combined with increasing biological oxygen production (9, 15)
427 and waning availability of residual reductants (e.g., Fe^{2+}), would have changed the marine
428 budgets of electron acceptors (e.g. sulfate; 51), curbing biogenic methane fluxes via enhanced
429 AOM (43), and ultimately changing the atmospheric response to biospheric stimulation (13,
430 15).

431 **HAZE FORMATION AS A HARBINGER OF PLANETARY OXIDATION?**

432 Biogenic methane production has been proposed as an efficient hydrogen shuttle to the
433 exosphere (41). Empirical studies throughout the solar system reveal that multiple processes
434 combine to enable hydrogen escape from the upper atmosphere at its maximum theoretical
435 rate (59), meaning that planetary hydrogen loss can be approximated by the diffusive supply
436 of H-bearing compounds from the stratosphere (e.g., H_2 , H_2O , CH_4). While freeze-distillation
437 confines water vapor to the troposphere, methane escapes Earth's cold-trap and supplies
438 hydrogen to the stratosphere through photolysis, which can be lost instantaneously to
439 space—irreversibly shedding reducing power and potentially explaining how the Earth's
440 surficial environment became irreversibly oxidized over long timescales (41, 59).

441 The abrupt change in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ correlated to a decrease in sedimentary $\delta^{13}\text{C}_{\text{Org}}$ seen in the C-
442 S anomaly (Figure 1B; 3) demonstrates a rapid change in atmospheric chemistry, which we
443 have interpreted to represent the development of a hydrocarbon haze formed at elevated
444 methane concentrations. As such, our data and models provide support for the presence of
445 substantial methane in the Archean atmosphere, confirming predictions made in multiple
446 theoretical studies (3, 20, 41-43, 47, 59). Our previous work (8, 9, 17, 18), and the work of
447 others (57), has shown that similar tandem decreases in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ and $\delta^{13}\text{C}_{\text{Org}}$ occur in other
448 Neoproterozoic strata, suggesting the Neoproterozoic atmospheric composition was dynamic, and
449 atmospheric haze development was potentially frequent in the overture to the GOE.
450 Experimental data (60, 61) and photochemical models (7, 9, 10, 20, 47) both predict that
451 hydrocarbon hazes form when $\text{CO}_2:\text{CH}_4$ mixing ratios exceed ~ 0.1 . Given the strong
452 dependency of hydrogen escape on atmospheric methane availability (41, 59), conceptually,

453 therefore, intervals of haze development could have served as intervals of heightened
454 hydrogen loss, implicating more reduced atmospheric chemistry as a harbinger of planetary
455 oxidation.

456 Catling *et al.* (41) performed three time-resolved calculations where they fixed $p\text{CO}_2$ (0.0003,
457 0.003 and 0.01 bar) and calculated the $p\text{CH}_4$ necessary to maintain a surface temperature of
458 290K against the evolving luminosity of the Archean sun. Using their Figure 1A, $p\text{CH}_4$ was
459 calculated to approximate 950, 170 and 130 ppm when $p\text{CO}_2$ was fixed at 0.0003, 0.003 and
460 0.01 bar. Simplifying atmospheric pressure to approximate 1 bar equates to background
461 $\text{CH}_4\text{:CO}_2$ mixing ratios of 3.16 (950 ppm/300 ppm), 0.06 (170 ppm/3000 ppm) and 0.01 (130
462 ppm/10000 ppm) for each scenario respectively. Excluding the first scenario because the
463 climatically necessitated $\text{CH}_4\text{:CO}_2$ mixing ratio requires the development of a potentially
464 improbably thick organic-haze (7, 9, 20, 47), leaves two clear skies solutions to explore.
465 Assuming organic-haze forms when the $\text{CH}_4\text{:CO}_2$ mixing ratio exceeds 0.1, haze development
466 in each scenario requires either a 1.67- (0.1/0.06) or 10- (0.1/0.01) fold increase in
467 atmospheric methane concentrations, or a factor of 1.5–10 increase in planetary oxidation
468 rate representing $2.6\text{--}18 \times 10^{12}$ moles O_2 equivalents yr^{-1} , assuming the background state was
469 $1\text{--}1.5 \times 10^{12}$ moles O_2 yr^{-1} . Consequently, given our estimate of haze duration (1.4 ± 0.4 Myr;
470 [SI Appendix](#)), a single episode of haze development could equate to a net gain of up to $\sim 2.6\text{--}$
471 18×10^{18} moles of O_2 equivalents to the Earth system (41).

472 It is important to stress that the absolute gain of oxygen equivalents, or the rate of hydrogen
473 loss, depends on both the composition of the atmosphere and on predictions of their resulting
474 climate. Catling *et al.* (41) utilized the climate model of Pavlov and Kasting (62), which has a
475 substantial error in the methane absorption coefficients as rectified by Haqq-Misra *et al.* (47).
476 When combined with more recent predictions of greenhouse and anti-greenhouse cooling
477 effects (63), Archean $p\text{CO}_2$ in excess of 0.01 is required to warm the planet in lieu of the lower
478 solar luminosity (47). A higher $p\text{CO}_2$ would reduce the background $\text{CH}_4\text{:CO}_2$ mixing ratio,
479 requiring a more substantial CH_4 flux to instigate haze formation. Logically, therefore, larger
480 fluxes of CH_4 would promote greater hydrogen escape rates, with concomitant greater
481 oxidative effect, rendering our estimates conservative. A more accurate and precise
482 treatment is dependent on emerging modeling approaches, incorporating more appropriate
483 particle physics and coupled climate modules to calculate accurate radiative transfer through
484 hazy atmospheres (63). However, for now, the most appropriate models reconcile haze
485 development with available geological evidence and suggest that run-away haze development
486 was inhibited by self-shielding (i.e., haze prevents methane photolysis), implicating intricate

487 feedback systems between biological methane production, atmospheric chemistry and
488 surface-incident UV radiation (63).

489 Assimilated, core GKF01 reveals a pronounced and stratigraphically systematic excursion
490 towards low $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ and $\delta^{13}\text{C}$ that requires a change in the composition of the atmosphere.
491 This contests the notion of homogenous atmospheric chemistry across vast swaths of Archean
492 time (64), while providing the strongest evidence to date that the Neoproterozoic was dynamic
493 on million-year time scales. These atmospheric oscillations are best explained via a strong
494 teleconnection between the biosphere and atmospheric chemistry, whereby increased
495 nutrient availability instigated a biogeochemical cascade, prompting organic-haze formation.
496 Episodic haze formation should have hastened hydrogen escape and likely acted as a counter-
497 intuitive mechanism of generating significant oxidizing equivalents to the whole Earth System
498 against an oxygen-free atmospheric backdrop.

499 **METHODS.** The geochemical data presented herein have been generated following
500 established methodologies. Similarly, the photochemical model has been updated, via the
501 inclusion of updated SO_2 -photodissociation cross-sections (33), from that developed in Claire
502 et al. (7). Here we précis our approach, reserving a complete description for the [SI Appendix](#).
503 Briefly: Sulfur isotope analysis was performed on purified SF_6 , following CRS pyrite distillation,
504 at the University of Maryland (8, 9). Analytical uncertainties are estimated from the long-term
505 reproducibility of Ag_2S fluorinations, and estimated to be 0.02, 0.008, and 0.20 ‰ (1 standard
506 deviation, 1σ) for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ ratios, respectively. Organic carbon isotope and TOC
507 data were generated at the JPL Astrobiogeochemistry Laboratory (abcLab) using 10 % (vol/vol)
508 HCl decarbonated sample residues. The average reproducibility of $\delta^{13}\text{C}_{\text{Org}}$ and TOC sample
509 duplicates was found to be ± 0.22 ‰ and 0.02 %, respectively. Iron speciation analyses were
510 conducted at the University of St. Andrews, exploiting an empirically calibrated sequential
511 extraction (65), as detailed in (66), with an extract precision of $\sim 5\%$ ([SI Appendix](#)).

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707

708 **Figure legends:**

709 **Figure 1 Pre-existing lithological and geochemical data from core GKF01 (9) combined with**
710 **new high-resolution geochemical data.** Panel **A** comprises the published low-resolution
711 GKF01 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ record (9), the Neoproterozoic reference array (red line) and its ± 0.1 uncertainty
712 envelope (grey vertical band; 8). Panel **B** features the new $\delta^{34}\text{S}$, $\Delta^{36}\text{S}/\Delta^{33}\text{S}$, $\delta^{13}\text{C}$, TOC and Fe-
713 speciation ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$, $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$) data (squares) along with published data (filled circles; 9, 15,
714 24). The horizontal grey band signifies the C-S anomaly (see text). The vertical red line and
715 grey envelope in the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ plot represent the Neoproterozoic reference array and its
716 associated uncertainty (± 0.1 ; 8). Vertical lines in the Fe-speciation plots distinguish oxic from
717 anoxic ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} \geq 0.38$) and ferruginous from definitively euxinic ($\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}} > 0.7$) water
718 column conditions. The open symbols in the $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{PY}}$ plot have $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} < 0.22$, signifying oxic
719 sedimentation (9, 15, 67). Assimilating these observations, sedimentation during the
720 examined interval was likely dynamic, with a generally ferruginous background state ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$
721 > 0.38 ; $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}} < 0.7$), becoming oxygenated during the C-S anomaly ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} < 0.22$; 15).
722 The definition of Fe_{HR} , Fe_{PY} and Fe_{T} are footnoted[‡], whereas the derivation of the diagnostic
723 Fe-speciation threshold values are given in the [SI Appendix](#). Analytical uncertainties (1
724 standard deviation, 1σ) are typically encompassed within each individual data point with the
725 exception of a few $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios whose uncertainty was computed from larger of the
726 internal or external 1σ uncertainties associated with the raw $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ data (9). The large-
727 scale lithological log (A) follows that presented in Zerkle *et al.* (9), whereas the new data (B)
728 are plotted against the detailed sedimentary logs, which along with core photos are available
729 online (<http://general.uj.ac.za/agouron/index.aspx>).

730 **Figure 2 Quadruple S-isotope data from core GKF01 (A) with a schematic mixing scenario**
731 **(B).** $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ trends for the new data (black and blue) superimposed on previously
732 published data (grey circles; 9). Regressions are given through the whole dataset (red) as well
733 as through the C-S anomaly (blue) and background (black). Uncertainties are plotted
734 conservatively, using the larger of the internal or external uncertainty (1σ), and are
735 consistently smaller than a single data point. The insert (B) schematically illustrates the range
736 of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values that can be expressed in pyrite (shaded grey area) formed via mixing
737 of sulfide derived from microbial sulfate reduction (open circles 3-4) with atmospherically
738 derived S-MIF carried by sulfate (filled circle 1) and elemental sulfur (filled circle 2). The
739 horizontal blue bar illustrates the $\Delta^{36}\text{S}-\Delta^{33}\text{S}$ systematics of TSR derived sulfide. Note, biological

740 activity has the potential to exert greater influence on $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ when pyrite carries a negative
741 $\Delta^{33}\text{S}$ (i.e. derived from sulfate) rather than a positive $\Delta^{33}\text{S}$ (29) as observed in the C-S anomaly
742 (Figure 1) and mixing with TSR derived sulfide moves the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ to less negative values.

743 **Figure 3 Carbon isotope ($\delta^{13}\text{C}$; A), TOC (B) and $\delta^{34}\text{S}$ (C) versus $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ data from 800–900**
744 **m core depth in core GKF01.** In each plot the data have been color coded, differentiating the
745 background (black) from the C-S anomaly (blue), with orange arrows illustrating its temporal
746 evolution. Vertical red lines in each plot give the average Neoproterozoic $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ with a ± 0.1
747 uncertainty envelope (vertical grey bar; 8). The horizontal green line in panel A marks $\delta^{13}\text{C} = -$
748 37‰ , a threshold commonly used to identify methanotrophy (8, 9, 26). The horizontal grey
749 bar in panel C represents the range of seawater $\delta^{34}\text{S}$ estimates derived from carbonate-d
750 associated sulfate (55). Typically analytical uncertainty is encompassed within the data points,
751 with the exception of a few $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios as in Figure 2.

752 **Figure 4 Photochemical $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ predictions for the “standard atmosphere” (7) under**
753 **normal conditions (A) and with differential sulfur loading (B).** Under standard atmospheric
754 conditions, in Figure 4A, sulfur leaves the model atmosphere unequally divided between three
755 exit channels (SO_2 , 56 %; S_8 , 24 % and SO_4 , 18 %). Values of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ are displayed for the
756 entire troposphere (filled circles), with the large squares showing the ground-level signal
757 carried by a specific exit channel combining both wet and dry deposition. Figure 4B recreates
758 the experiment illustrated in Figures 6c–d in Claire et al. (7), where the total volcanic sulfur
759 flux to the model atmosphere is varied over two orders of magnitude (10^8 – 10^{10} molecules $^{-2}$ s $^{-1}$
760 1). The spatial distribution of atmospherically important species within the standard
761 atmospheric framework is displayed in Figure 2 of Claire et al. (7) where the following
762 boundary conditions were adopted: volcanic sulfur flux of 3.85×10^9 molecules cm^{-2} s $^{-1}$ (1
763 Tmole a $^{-1}$) at an $\text{H}_2\text{S}:\text{SO}_2$ ratio of 1:10 and a volcanic H_2 flux of 1×10^{10} molecules cm^{-2} s $^{-1}$ (3
764 Tmole a $^{-1}$). Fixed ground-level mixing ratios of 100 ppm and 10 ppb for CH_4 and O_2 ,
765 respectively. Carbon dioxide concentrations were fixed at 1 % at all heights and N_2 provided
766 a total atmospheric pressure of 1 bar. Full details of the model, validation and its limitations
767 are given in the SI Appendix.

768 **Figure 5 Simulated $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ response to varying O_2 and CH_4 fluxes.** Figure 5A shows the
769 three distinct atmospheric states (Models 1–3, Figures 5B–5D) that were chosen to examine
770 the effect of a hydrocarbon haze on atmospheric chemistry (numbered vertical grey bands
771 Figure 5A): The first model simulates a thick hydrocarbon haze prior to the advent of oxygenic
772 photosynthesis (Figure 5B), whereas the second and third models represent haze-free (Figure
773 5C) and hazy (Figure 5D) states after the advent of oxygenic photosynthesis (7, 10). Under

774 each atmospheric regime (Figures 5B–5D) the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ carried by each atmospheric exit
775 channel, at specific atmospheric height, is plotted as color-coded circles, whereas the
776 atmospherically integrated signal (the ground-level value) of each vector is represented by a
777 color-coded large square (Plots B–D). The relative importance of each exit labeled channel is
778 given in parenthesis. In plot A the mixing ratios of atmospheric species are shown as solid lines
779 (left axis), while fluxes are shown as dashed lines (right axis). In Figure 5B–5D the Archean
780 reference array ($\Delta^{36}\text{S}/\Delta^{33}\text{S} = -0.9; 8$), the steepened slope reflecting the C-S anomaly (Figure
781 1) and the best fit to the simulated data are given by the dotted, dot-dashed and solid lines
782 respectively. Full details of the model, validation and its limitations are given in the SI
783 Appendix. Zero $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ data are given as grey lines to illustrate the change in scale
784 between Figure 5B–D.

785