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# Biological Regulation of Atmospheric Chemistry En Route to Planetary Oxygenation

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

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

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

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

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

**SIGNIFICANCE STATEMENT:** It has been proposed that enhanced methane fluxes to Earth’s early atmosphere could have altered atmospheric chemistry, initiating a hydrocarbon-rich haze reminiscent of Saturn’s moon, Titan. The occurrence, cause and significance of haze development, however, remain unknown. Here, we test and refine the “haze hypothesis” by combining an ultra-high-resolution sulfur- and carbon-isotope dataset with photochemical simulations to reveal the structure and timing of haze development. These data suggest that haze persisted for  $\sim 1$  Myr, requiring a sustained biological driver. We propose that enhanced atmospheric  $\text{CH}_4$ , implied by the presence of haze, could have had a significant impact on the escape of hydrogen from the atmosphere, effectively contributing to the terminal oxidation of Earth’s surficial environments at  $\sim 2.4$  Ga.

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## INTRODUCTION

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

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

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<sup>1</sup> Sulfur-isotope ratios are conventionally reported in delta ( $\delta$ ) notation, and reflect the permil (‰) deviation of the ratio of the least abundant ( $^{33}\text{S}$ ,  $^{34}\text{S}$ ,  $^{36}\text{S}$ ) to the most isotope ( $^{32}\text{S}$ ) 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 ( $\Delta$ ) 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  $\Delta^{36}\text{S}$  [ $((^{36}\text{S}/^{32}\text{S})_{\text{sample}} / (^{36}\text{S}/^{32}\text{S})_{\text{V-CDT}}) - ((^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{V-CDT}})^{1.9}$ ].

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

## RESULTS

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

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

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

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

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

## DISCUSSION

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

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

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

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

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

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

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

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

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

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

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

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 site of methane production/consumption was occurring elsewhere.

To examine the direct link between  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  values and atmospheric chemistry, we updated 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 through an atmospheric reaction network. Details of the model and our preliminary validation approach are provided in the [SI Appendix](#). The most significant changes from the initial predictions of Claire et al. (7) arise from the inclusion of new data allowing  $\Delta^{36}\text{S}$  predictions, and the use of newly measured  $\text{SO}_2$  photodissociation cross-sections (33). As noted previously (7, 34), the earlier  $\text{SO}_2$  cross-sections (35) produced results at odds to the commonly accepted interpretation of the geologic record: predicting positive  $\Delta^{33}\text{S}$  in sulfate and negative  $\Delta^{33}\text{S}$  in elemental sulfur. Incorporating the revised cross-sections (33) resolve this data-model mismatch, and now predict exit channels with the arithmetic sign commonly seen in the rock record ([Figures 4–5](#)). However, it is important to note our model still fails to reproduce both the magnitude of the S-MIF and the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratio archived in the geological record ([Figures 1, 4–5; S SI Appendix](#)). A detailed exploration of this discrepancy exceeds the scope of this study, but likely reflects uncertainties concerning the primary S-MIF generating mechanism(s) included within the model and/or the composition of the Archean background state ([Figure 4; 7](#)). Both of these potential sources of uncertainty are the focus of on-going research and remain fundamental to successful inverse reconstruction of the Archean atmosphere.

[Figure 4A](#) provides insight into the transmittance of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios through an atmospheric reaction network. Exploiting the putative Neoproterozoic atmospheric composition (the “standard model”) envisaged by Claire et al (7), sulfur-species leave the atmosphere unequally divided between three exit channels. The model predicts that aerosol exit channels ( $\text{SO}_4$  and  $\text{S}_8$ ) feature fairly homogeneous  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  signatures irrespective of the height of their tropospheric genesis. By contrast, the predicted  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios communicated to  $\text{SO}_2$  vary substantially through the troposphere.  $\text{SO}_2$  exits the atmosphere primarily dissolved in rainwater, so homogenization likely precludes the expression of the modeled  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  variability ([Figures 4–5](#)). Aerosol species, by contrast, should serve as more instantaneous vectors carrying the entire range of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  to the Earth’s surface, resulting in spatial variability independent of atmospheric chemistry. Consequently, the modeled  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  stability in aerosols is reassuring, advocating  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios as a conservative parameter reflective of a given atmospheric state; that, unlike the absolute S-MIF magnitude (32), would be unlikely to display significant widespread spatial variability under a truly global atmospheric state. This fits well with the stable background  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  (-0.9) that is observed

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

The utility of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios is extended via examination of [Figure 4B](#). Here, we present results from 22 distinct model atmospheres where the total volcanic sulfur flux was varied over two orders of magnitude. This experiment alters the atmospheric redox state, enhancing the relative importance of the  $\text{S}_8$  exit-channel in the more sulfur-laden atmospheres. [Figure 4B](#) shows that within each model atmosphere the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios of all exit-channels remain homogenous ( $\pm 0.1$ ), in-turn supporting our claim that  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  reflects the instantaneous state of atmospheric chemistry. The range and systematic decrease in  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  observed between simulations (+0.2 to -0.4) highlights the sensitivity of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios to atmospheric composition, advocating  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  as a promising atmospheric probe—A conclusion that extends beyond both the chosen experiment (sulfur loading) and our predicted magnitudes.

To examine the ability of an organic haze to modulate  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ , we varied the  $\text{O}_2$  and  $\text{CH}_4$  fluxes (7, 10) to create two different hazy states, ([Models 1 & 3 in Figure 5B & 5D](#)) along with an additional clear-skies atmospheric state ([Model 2 in Figure 5C](#)). Similar to the cases presented previously ([Figure 4A](#)), the incorporation of the new cross-sections (33) causes the  $\Delta^{33}\text{S}$  predictions to deviate from those presented previously (7), qualitatively approximating the geological record. Our simulated hazy atmospheric states produce  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slopes (+0.19, [Figure 5B](#) and -0.52, [Figure 5D](#)), which differ from the clear-skies simulation (-0.04, [Figure 5C](#)). The clear-skies simulation in [Figure 5C](#) has distinct, but broadly similar, boundary conditions to the “standard atmosphere” ([Figure 4A](#); 7) so their similar  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  provides additional confidence that  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slopes are the product of specific atmospheric states, and do not vary widely with minor fluctuations in atmospheric state. We stress again that the absolute values of these predictions are preliminary and will likely change with additional model complexity ([SI Appendix](#)). Our approach here is not sufficient to make the claim that haze is uniquely responsible for variations in the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope from -0.9 to -1.5. Rather, our more simple aim is to test the assertion that atmospheric reaction rates, exit channels and UV transparency vary sufficiently underneath a hazy atmosphere to modulate the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios (7-10). The predicted uniformity of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios, expressed in all atmospheric exit channels, ultimately facilitates transmission from the atmosphere where they may be preserved in the geological record (8, 9, 18)—a key prediction of the haze hypothesis. Furthermore, the different  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios produced under different atmospheric hazy regimes provides support to the idea that hazes in different parts of Earth history (e.g., before

and after substantial biospheric O<sub>2</sub> fluxes) might yield unique S-MIF signatures (cf. [Figures 5B and 5D](#); 8).

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

## CONSTRAINING THE TIMING AND DRIVERS OF ATMOSPHERIC HAZE FORMATION

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

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

or by a consortium of anaerobic methanotrophs and sulfate reducers (AOM) at the sulfate-methane transition zone (41-43). Nevertheless, within the oxygen- and sulfate-starved Neoproterozoic oceans (44-46) methanogens would have proliferated, whilst methanotrophs and AOM would have been spatially restricted. Correspondingly, enhanced Neoproterozoic methanogenesis would have likely translated into elevated atmospheric CH<sub>4</sub> fluxes (41-43), supporting large background Archean CH<sub>4</sub> concentrations (7, 10, 20, 21, 41, 47). When the CH<sub>4</sub>:CO<sub>2</sub> mixing ratio exceeded a critical threshold of ~ 0.1, this CH<sub>4</sub> flux would have formed an organic-rich hydrocarbon haze (9, 10, 20, 47), although the regional/global extent of these haze(s) require further study.

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

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

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<sup>3</sup> Summation of the oxic (Fe<sub>Carb</sub>, Fe<sub>Ox</sub> and Fe<sub>Mag</sub>) and anoxic Fe extractions (Fe<sub>Py</sub>) defines the highly reactive Fe pool (Fe<sub>HR</sub> = Fe<sub>Carb</sub> + Fe<sub>Ox</sub> + Fe<sub>Mag</sub> + Fe<sub>Py</sub>), which when normalized to the total Fe pool (Fe<sub>T</sub>) and Fe<sub>Py</sub> permits distinction between oxic (Fe<sub>HR</sub>/Fe<sub>T</sub> =  $< 0.22$ ), ferruginous (Fe<sub>HR</sub>/Fe<sub>T</sub> =  $> 0.38$  and Fe<sub>Py</sub>/Fe<sub>HR</sub> =  $< 0.7$ ) and euxinic Fe<sub>HR</sub>/Fe<sub>T</sub> =  $> 0.38$  and Fe<sub>Py</sub>/Fe<sub>HR</sub> =  $> 0.8$ ) depositional conditions. Details of mineral phases that comprise these operationally defined

(9, 15), arguing against a preservational control. Contrasting redox inferences gleaned from the S-MIF and the Fe-speciation records further implicate marine productivity with atmospheric haze development. Here the low  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  ( $< 0.38$ ) ratios, in concert with limited enrichments in redox sensitive trace metals (e.g. Mo, Re and U; 15), signal mildly oxic sedimentation against an anoxic atmospheric backdrop (Figure 1b). Given that atmospheric models insinuate  $\text{O}_2$  residence times on the order of a few hours (7) and extremely reducing tropospheric conditions, these data can only be reconciled by oxygenic photosynthesis (15) creating locally oxygenated water column conditions and the development of an oxygen oasis (52). The production of oxygen and organic matter in surface environments and their destruction in deeper waters, the sediment–water interface and below, had the potential to spatially decouple oxygen and methane production; thereby, offering a mechanism where methane could have escaped water column reoxidation and contributed to the atmospheric methane burden.

Excluding a facies control on the observed TOC increase is more difficult. The deepening experienced during the mudstone deposition probably inhibited carbonate deposition via isolation from the photic zone (23), hence reducing the dilutive effects of the biogenic carbonates during the C-S anomaly. That said, the small-intercalated mudstones in the basal part of the examined section ( $< 840$  m) represent the same facies change, yet do not display the isotopic covariation that defines the C-S anomaly. This difference we explain as a function of scale: The mudstone containing the C-S anomaly has known lateral facies equivalents in core GKP01 (15, 23, 53), so independent of dilution-type effects, TOC-rich sediments were deposited across a larger area of the Griqualand West basin during the C-S anomaly. Thus increased TOC deposition could have supplied ample organic carbon to fuel regionally pervasive methanogenesis, potentially enhancing methane fluxes to the atmosphere. Importantly, consistent with the predictions of atmospheric simulations (7), the persistence of large magnitude S-MIF with changing  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  (Figure 2; SI Appendix, Fig. S1) demonstrates that the atmosphere remained essentially oxygen free (1-3, 6, 7, 10) despite evidence for enhanced oxygen production (9, 15). Apparently the global sinks of water column reductants (e.g.  $\text{Fe}^{2+}$ ; 4), combined with reduced atmospheric gases (e.g.,  $\text{H}_2$ ,  $\text{CH}_4$ ), were still sufficient to prevent atmospheric oxygenation at this time (7, 10).

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

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

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

Pyrite  $\delta^{34}\text{S}$  values are lowest at the base of the C-S anomaly (~ -15 ‰) before stabilizing to values close to those reconstructed from contemporaneous carbonate-associated sulfate from the Campbellrand carbonate platform (Figures 1, 3C; 55;). While these few  $^{34}\text{S}$  depleted samples could easily reflect changes in sediment-housed microbial sulfur cycling and associated pyrite formation (19, 56), these data can also be reconciled with an initial weathering pulse delivering sulfate, and presumably other nutrients, to the biosphere. Beyond the fortuitous placement of the low  $\delta^{34}\text{S}$  at the base of the C-S anomaly within an otherwise stable  $\delta^{34}\text{S}$  record (Figures 1, 3C), unequivocal discrimination between these two potential explanations of the  $\delta^{34}\text{S}$  data is challenging on the basis of bulk SF<sub>6</sub> measurements alone. Enigmatically, however, radiogenic  $^{187}\text{Os}/^{188}\text{Os}_i$  ratios have recently been reported from the Mt. McRae shale, which can only be reconciled with crustal  $^{187}\text{Os}$  ingrowth via  $\beta^-$ -decay of  $^{187}\text{Re}$ , followed by remobilization and delivery to the marine reservoir (14). The Mt. McRae succession is perhaps one of the most celebrated Archean sedimentary successions, containing the ~2.5 Ga trace-element enrichments that were interpreted to represent pre-GOE whiffs of oxygen (13). Interestingly, as noted by Zerkle et al. (9), the upper Mt. McRae shale also features a change in  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  to lower values (57), which is broadly associated with a change in  $\delta^{13}\text{C}_{\text{Org}}$ —exhibiting some interesting parallels with the data presented herein. Unfortunately the Mt. McRae shale data are of insufficient resolution to make meaningful comparisons with our own, and no Re-Os data exist for the C-S anomaly examined in Figure 1. Clearly further targeted SF<sub>6</sub> and SIMS analysis, coupled with the application of sensitive radiogenic isotope tracers (e.g. Re-Os; 58), to this and other C-S anomalies (8, 9), has the potential to elucidate the source of the nutrients (weathering vs. oceanic nutrient redistribution) and should be a fruitful avenue of future research.

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

pile and enter the atmosphere. The Neoarchean oceans as a whole are inferred to have had historically low sulfate concentrations (16, 45), poisoning the biosphere at a tipping point, allowing the balance between methane production and consumption to shift rapidly following pulses of marine fertilization and attendant sedimentary carbon delivery (8). Consequently, enhanced productivity would be expected to strengthen methane production, creating 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 methane fluxes are sufficient to affect atmospheric chemistry. Eventually, however, enhanced terrestrial colonization (51, 54), combined with increasing biological oxygen production (9, 15) and waning availability of residual reductants (e.g.,  $\text{Fe}^{2+}$ ), would have changed the marine budgets of electron acceptors (e.g. sulfate; 51), curbing biogenic methane fluxes via enhanced AOM (43), and ultimately changing the atmospheric response to biospheric stimulation (13, 15).

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

Biogenic methane production has been proposed as an efficient hydrogen shuttle to the exosphere (41). Empirical studies throughout the solar system reveal that multiple processes combine to enable hydrogen escape from the upper atmosphere at its maximum theoretical rate (59), meaning that planetary hydrogen loss can be approximated by the diffusive supply of H-bearing compounds from the stratosphere (e.g.,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ). While freeze-distillation confines water vapor to the troposphere, methane escapes Earth's cold-trap and supplies hydrogen to the stratosphere through photolysis, which can be lost instantaneously to space—irreversibly shedding reducing power and potentially explaining how the Earth's surficial environment became irreversibly oxidized over long timescales (41, 59).

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-S anomaly (Figure 1B; 3) demonstrates a rapid change in atmospheric chemistry, which we have interpreted to represent the development of a hydrocarbon haze formed at elevated methane concentrations. As such, our data and models provide support for the presence of substantial methane in the Archean atmosphere, confirming predictions made in multiple theoretical studies (3, 20, 41-43, 47, 59). Our previous work (8, 9, 17, 18), and the work of 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 Neoarchean strata, suggesting the Neoarchean atmospheric composition was dynamic, and atmospheric haze development was potentially frequent in the overture to the GOE. Experimental data (60, 61) and photochemical models (7, 9, 10, 20, 47) both predict that hydrocarbon hazes form when  $\text{CO}_2:\text{CH}_4$  mixing ratios exceed  $\sim 0.1$ . Given the strong dependency of hydrogen escape on atmospheric methane availability (41, 59), conceptually,

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

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

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

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

Assimilated, core GKF01 reveals a pronounced and stratigraphically systematic excursion 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. This contests the notion of homogenous atmospheric chemistry across vast swaths of Archean time (64), while providing the strongest evidence to date that the Neoarchean was dynamic on million-year time scales. These atmospheric oscillations are best explained via a strong teleconnection between the biosphere and atmospheric chemistry, whereby increased nutrient availability instigated a biogeochemical cascade, prompting organic-haze formation. Episodic haze formation should have hastened hydrogen escape and likely acted as a counter-intuitive mechanism of generating significant oxidizing equivalents to the whole Earth System against an oxygen-free atmospheric backdrop.

**METHODS.** The geochemical data presented herein have been generated following established methodologies. Similarly, the photochemical model has been updated, via the inclusion of updated  $\text{SO}_2$ -photodissociation cross-sections (33), from that developed in Claire et al. (7). Here we précis our approach, reserving a complete description for the [SI Appendix](#). Briefly: Sulfur isotope analysis was performed on purified  $\text{SF}_6$ , following CRS pyrite distillation, at the University of Maryland (8, 9). Analytical uncertainties are estimated from the long-term reproducibility of  $\text{Ag}_2\text{S}$  fluorinations, and estimated to be 0.02, 0.008, and 0.20 ‰ (1 standard deviation,  $1\sigma$ ) for  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$  ratios, respectively. Organic carbon isotope and TOC data were generated at the JPL Astrobiogeochemistry Laboratory (abcLab) using 10 % (vol/vol) HCl decarbonated sample residues. The average reproducibility of  $\delta^{13}\text{C}_{\text{Org}}$  and TOC sample duplicates was found to be  $\pm 0.22$  ‰ and 0.02 %, respectively. Iron speciation analyses were conducted at the University of St. Andrews, exploiting an empirically calibrated sequential extraction (65), as detailed in (66), with an extract precision of  $\sim 5\%$  ([SI Appendix](#)).

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## References

1. Farquhar J, Bao H, & Thiemens M (2000) Atmospheric Influence of Earth's Earliest Sulfur Cycle. *Science* 289(5480):756-758.
2. Farquhar J, Savarino J, Airieau S, & Thiemens MH (2001) Observation of wavelength-sensitive mass-independent sulfur isotope effects during SO<sub>2</sub> photolysis: Implications for the early atmosphere. *J. Geophys. Res-Planets* 106(E12):32829-32839.
3. Pavlov AA & Kasting JF (2002) Mass-Independent Fractionation of Sulphur Isotopes in Archean Sediments: Strong evidence for an Anoxic Archean Atmosphere. *Astrobiology* 2(1):27-41.
4. Holland HD (2006) The oxygenation of the atmosphere and oceans. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 361(1470):903-915.
5. Bekker A, *et al.* (2004) Dating the rise of atmospheric oxygen. *Nature* 427(6970):117-120.
6. Farquhar J, Zerkle AL, & Bekker A (2011) Geological constraints on the origin of oxygenic photosynthesis. *Photosyn. Res.* 107(1):11-36.
7. Claire MW, *et al.* (2014) Modeling the signature of sulfur mass-independent fractionation produced in the Archean atmosphere. *Geochim. Cosmochim. Acta* 141:365-380.
8. Izon G, *et al.* (2015) Multiple oscillations in Neoarchaeon atmospheric chemistry. *Earth Planet. Sci. Lett.* 431:264-273.
9. Zerkle AL, Claire MW, Domagal-Goldman SD, Farquhar J, & Poulton SW (2012) A bistable organic-rich atmosphere on the Neoarchaeon Earth. *Nat. Geosci.* 5(5):359-363.
10. Kurzwil F, *et al.* (2013) Atmospheric sulfur rearrangement 2.7 billion years ago: Evidence for oxygenic photosynthesis. *Earth Planet. Sci. Lett.* 366:17-26.
11. Guo Q, *et al.* (2009) Reconstructing Earth's surface oxidation across the Archean-Proterozoic transition. *Geology* 37(5):399-402.
12. Luo G, *et al.* (2016) Rapid oxygenation of Earth's atmosphere 2.33 billion years ago. *Sci. Adv.* 2(5).
13. Anbar AD, *et al.* (2007) A Whiff of Oxygen Before the Great Oxidation Event? *Science* 317(5846):1903-1906.
14. Kendall B, Creaser RA, Reinhard CT, Lyons TW, & Anbar AD (2015) Transient episodes of mild environmental oxygenation and oxidative continental weathering during the late Archean. *Sci. Adv.* 1(10).
15. Kendall B, *et al.* (2010) Pervasive oxygenation along late Archean ocean margins. *Nat. Geosci.* 3(9):647-652.
16. Crowe SA, Dossing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., Canfield, D.E. (2013) Atmospheric oxygenation three billion years ago. *Nature* 501:535-538.
17. Williford KH, *et al.* (2016) Carbon and sulfur isotopic signatures of ancient life and environment at the microbial scale: Neoarchean shales and carbonates. *Geobiology* 14(2):105-128.
18. Farquhar J, Cliff, J., Zerkle, A.L., Kamyshny, A., and Poulton, S.W., Claire, M., Adams, D., Harms, B. (2013) Pathways for Neoarchean pyrite formation constrained by mass-independent sulfur isotopes. *Proc. Natl. Acad. Sci. U.S.A.* 110(44):17638-17643.
19. Johnston DT (2011) Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle. *Earth-Sci. Rev.* 106(1-2):161-183.
20. Domagal-Goldman SD, Kasting JF, Johnston DT, & Farquhar J (2008) Organic haze, glaciations and multiple sulfur isotopes in the Mid-Archean Era. *Earth Planet. Sci. Lett.* 269(1-2):29-40.

- 566 21. Zahnle K, Claire M, & Catling D (2006) The loss of mass-independent fractionation in sulfur due  
567 to a Palaeoproterozoic collapse of atmospheric methane. *Geobiology* 4(4):271-283.
- 568 22. Thomazo C, Nisbet EG, Grassineau NV, Peters M, & Strauss H (2013) Multiple sulfur and carbon  
569 isotope composition of sediments from the Belingwe Greenstone Belt (Zimbabwe): A biogenic  
570 methane regulation on mass independent fractionation of sulfur during the Neoproterozoic?  
571 *Geochim. Cosmochim. Acta* 121(0):120-138.
- 572 23. Schröder S, Lacassie, J.P., Beukes, N.J., (2006) Stratigraphic and geochemical framework of the  
573 Agouron drill cores, Transvaal Supergroup (Neoproterozoic-Paleoproterozoic, South Africa). *S. Afr.*  
574 *J. Geol.* 109:23-54.
- 575 24. Ono SH, Kaufman AJ, Farquhar J, Sumner DY, & Beukes NJ (2009) Lithofacies control on  
576 multiple-sulfur isotope records and Neoproterozoic sulfur cycles. *Precambrian Res.* 169: 58-67.
- 577 25. Ono S, *et al.* (2003) New insights into Archean sulfur cycle from mass-independent sulfur  
578 isotope records from the Hamersley Basin, Australia. *Earth Planet Sci. Lett.* 213(1–2):15-30.
- 579 26. Eigenbrode JL & Freeman KH (2006) Late Archean rise of aerobic microbial ecosystems. *Proc.*  
580 *Natl. Acad. Sci. U.S.A* 103(43):15759-15764.
- 581 27. Thomazo C, Ader M, Farquhar J, & Philippot P (2009) Methanotrophs regulated atmospheric  
582 sulfur isotope anomalies during the Mesoproterozoic (Tumbiana Formation, Western Australia).  
583 *Earth Planet Sci. Lett.* 279(1–2):65-75.
- 584 28. Ono S, Wing B, Johnston D, Farquhar J, & Rumble D (2006) Mass-dependent fractionation of  
585 quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles.  
586 *Geochim. Cosmochim.* 70(9):2238-2252.
- 587 29. Roerdink DL, Mason PRD, Whitehouse MJ, & Brouwer FM (2016) Reworking of atmospheric  
588 sulfur in a Paleoproterozoic hydrothermal system at Londozi, Barberton Greenstone Belt,  
589 Swaziland. *Precambrian Res.* 280:195-204.
- 590 30. Canfield DE, Farquhar J, & Zerkle AL (2010) High isotope fractionations during sulfate reduction  
591 in a low-sulfate euxinic ocean analog. *Geology* 38(5):415-418.
- 592 31. Oduro H, *et al.* (2011) Evidence of magnetic isotope effects during thermochemical sulfate  
593 reduction. *Proc. Natl. Acad. Sci. U.S.A* 108(43):17635-17638.
- 594 32. Halevy I (2013) Production, preservation, and biological processing of mass-independent  
595 sulfur isotope fractionation in the Archean surface environment. *Proc. Natl. Acad. Sci. U.S.A*  
596 110(44):17644-17649.
- 597 33. Endo Y, *et al.* (2015) Photoabsorption cross-section measurements of <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S sulfur  
598 dioxide from 190 to 220 nm. *J Geophys. Res-Atmos.* 120(6):2546-2557.
- 599 34. Lyons JR (2009) Atmospherically-derived mass-independent sulfur isotope signatures, and  
600 incorporation into sediments. *Chem. Geol.* 267(3–4):164-174.
- 601 35. Danielache SO, Eskebjerg C, Johnson MS, Ueno Y, & Yoshida N (2008) High-precision  
602 spectroscopy of <sup>32</sup>S, <sup>33</sup>S, and <sup>34</sup>S sulfur dioxide: Ultraviolet absorption cross sections and  
603 isotope effects. *J Geophys. Res-Atmos.* 113(D17):D17314.
- 604 36. Knoll AH & Beukes NJ (2009) Introduction: Initial investigations of a Neoproterozoic shelf margin-  
605 basin transition (Transvaal Supergroup, South Africa). *Precambrian Res.* 169(1–4):1-14.
- 606 37. Altermann W & Nelson DR (1998) Sedimentation rates, basin analysis and regional correlations  
607 of three Neoproterozoic and Palaeoproterozoic sub-basins of the Kaapvaal craton as inferred  
608 from precise U–Pb zircon ages from volcanoclastic sediments. *Sediment. Geol.* 120(1–4):225-  
609 256.
- 610 38. Barton ES, Altermann, W., Williams, I.S., Smith, C.B., (1994) U–Pb zircon age for a tuff in the  
611 Campbell Group, Griqualand West Sequence, South Africa: implications for early Proterozoic  
612 rock accumulation rates. *Gology* 22:343–346.

- 613 39. Gutzmer J & Beukes NJ (1998) High-grade manganese ores in the Kalahari manganese field:  
614 Characterization and dating of the ore forming events. in *Unpublished Report*, (Rand Afrikaans  
615 University, Johannesburg), p 221.
- 616 40. Sumner DY & Bowring SA (1996) U–Pb geochronologic constraints on deposition of the  
617 Campbellrand Subgroup, Transvaal Supergroup, South Africa. *Precambrian Res.* 79(1–2):25–  
618 35.
- 619 41. Catling DC, Zahnle KJ, & McKay CP (2001) Biogenic Methane, Hydrogen Escape, and the  
620 Irreversible Oxidation of Early Earth. *Science* 293(5531):839–843.
- 621 42. Kharecha P, Kasting J, & Siefert J (2005) A coupled atmosphere–ecosystem model of the early  
622 Archean Earth. *Geobiology* 3(2):53–76.
- 623 43. Beal EJ, Claire MW, & House CH (2011) High rates of anaerobic methanotrophy at low sulfate  
624 concentrations with implications for past and present methane levels. *Geobiology* 9(2):131–  
625 139.
- 626 44. Crowe SA, *et al.* (2014) Sulfate was a trace constituent of Archean seawater. *Science*  
627 346(6210):735–739.
- 628 45. Zhelezinskaia I, Kaufman AJ, Farquhar J, & Cliff J (2014) Large sulfur isotope fractionations  
629 associated with Neoarchean microbial sulfate reduction. *Science* 346(6210):742–744.
- 630 46. Guy BM, *et al.* (2012) A multiple sulfur and organic carbon isotope record from non-  
631 conglomeratic sedimentary rocks of the Mesoarchean Witwatersrand Supergroup, South  
632 Africa. *Precambrian Res.* 216–219:208–231.
- 633 47. Haqq-Misra JD, Domagal-Goldman SD, Kasting PJ, & Kasting JF (2008) A revised, hazy methane  
634 greenhouse for the Archean Earth. *Astrobiology* 8(6):1127–1137.
- 635 48. da Silva JJRF & Williams RJP (1991) *The Biological Chemistry of the Elements: The Inorganic*  
636 *Chemistry of Life* (Oxford University Press).
- 637 49. Konhauser KO, *et al.* (2009) Oceanic nickel depletion and a methanogen famine before the  
638 Great Oxidation Event. *Nature* 458(7239):750–753.
- 639 50. Konhauser KO, *et al.* (2015) The Archean Nickel Famine Revisited. *Astrobiology* 15(10):804–  
640 815.
- 641 51. Stüeken EE, Catling DC, & Buick R (2012) Contributions to late Archaean sulphur cycling by life  
642 on land. *Nat. Geosci.* 5(10):722–725.
- 643 52. Olson SL, Kump LR, & Kasting JF (2013) Quantifying the areal extent and dissolved oxygen  
644 concentrations of Archean oxygen oases. *Chem. Geol.* 362:35–43.
- 645 53. Sumner DY & Beukes NJ (2006) Sequence stratigraphic development of the Neoarchean  
646 Transvaal carbonate platform, Kaapvaal Craton, South Africa. *S. Afri. J. Geol.* 109:11–22.
- 647 54. Lalonde SV & Konhauser KO (2015) Benthic perspective on Earth’s oldest evidence for oxygenic  
648 photosynthesis. *Proc. Natl. Acad. Sci. U.S.A* 112(4):995–1000.
- 649 55. Paris G, Adkins JF, Sessions AL, Webb SM, & Fischer WW (2014) Neoarchean carbonate–  
650 associated sulfate records positive  $\Delta 33\text{S}$  anomalies. *Science* 346(6210):739–741.
- 651 56. Bradley AS, *et al.* (2016) Patterns of sulfur isotope fractionation during microbial sulfate  
652 reduction. *Geobiology* 14(1):91–101.
- 653 57. Kaufman AJ, *et al.* (2007) Late Archean Biospheric Oxygenation and Atmospheric Evolution.  
654 *Science* 317(5846):1900–1903.
- 655 58. Cohen AS (2004) The rhenium–osmium isotope system: applications to geochronological and  
656 palaeoenvironmental problems. *J. Geol. Soc. London* 161(4):729–734.
- 657 59. Zahnle KJ, Catling DC, & Claire MW (2013) The rise of oxygen and the hydrogen hourglass.  
658 *Chem. Geol.* 362:26–34.

- 659 60. Trainer MG, *et al.* (2006) Organic haze on Titan and the early Earth. *Proc. Natl. Acad. Sci. U.S.A*  
660 103(48):18035-18042.
- 661 61. Hasenkopf CA, *et al.* (2010) Optical properties of Titan and early Earth haze laboratory analogs  
662 in the mid-visible. *Icarus* 207(2):903-913.
- 663 62. Pavlov AA, Kasting JF, Brown LL, Rages KA, & Freedman R (2000) Greenhouse warming by CH<sub>4</sub>  
664 in the atmosphere of early Earth. *J. Geophys Res-Planets* 105(E5):11981-11990.
- 665 63. Arney G, Domagal-Goldman, S., Meadows, V., Wolf, E., Schwieterman, E., Charnay, B.,  
666 Hebrard, E., Trainer, M. & Claire, M (2016) The Pale Orange Dot: The spectrum and habitability  
667 of hazy Archean Earth. *Astrobiology* 16(11):1-27.
- 668 64. Thomassot E, O'Neil J, Francis D, Cartigny P, & Wing BA (2015) Atmospheric record in the  
669 Hadean Eon from multiple sulfur isotope measurements in Nuvvuagittuq Greenstone Belt  
670 (Nunavik, Quebec). *Proc. Natl. Acad. Sci. U.S.A* 112(3):707-712.
- 671 65. Poulton SW & Canfield DE (2005) Development of a sequential extraction procedure for iron:  
672 implications for iron partitioning in continentally derived particulates. *Chem. Geol.* 214(3-  
673 4):209-221.
- 674 66. Poulton, SW, Fralick, PW, Canfield, DE, (2010) Spatial variability in oceanic redox structure 1.8  
675 billion years ago. *Nat. Geosci.* 3:486-490.
- 676 67. Poulton SW & Canfield DE (2011) Ferruginous Conditions: A Dominant Feature of the Ocean  
677 through Earth's History. *Elements* 7(2):107-112.
- 678 68. Fischer WW, *et al.* (2009) Isotopic constraints on the Late Archean carbon cycle from the  
679 Transvaal Supergroup along the western margin of the Kaapvaal Craton, South Africa.  
680 *Precambrian Res.* 169(1-4):15-27.
- 681 69. Eriksson PG, Altermann W, & Hartzer FJ (2006) *The Geology of South Africa*, (eds) Johnson MR,  
682 Anhaeusser, C.R., and Thomas, R.J. Geological Society of South Africa, Johannesburg/Council  
683 for Geoscience, Pretoria, pp 237-260.
- 684 70. Canfield DE, Raiswell R, Westrich JT, Reaves CM, & Berner RA (1986) The use of chromium  
685 reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem. Geol.*  
686 54(1-2):149-155.
- 687 71. Clarkson MO, Poulton SW, Guilbaud R, & Wood RA (2014) Assessing the utility of Fe/Al and Fe-  
688 speciation to record water column redox conditions in carbonate-rich sediments. *Chem. Geol.*  
689 382:111-122.
- 690 72. Raiswell R & Canfield DE (1998) Sources of iron for pyrite formation in marine sediments. *Am.*  
691 *J. Sci.* 298(3):219-245.
- 692 73. Anderson TF & Raiswell R (2004) Sources and mechanisms for the enrichment of highly  
693 reactive iron in euxinic Black Sea sediments. *Am. J. Sci.* 304(3):203-233.
- 694 74. Poulton SW & Raiswell R (2002) The low-temperature geochemical cycle of iron: From  
695 continental fluxes to marine sediment deposition. *Am. J. Sci.* 302(9):774-805.
- 696 75. Cumming VM, Poulton SW, Rooney AD, & Selby D (2013) Anoxia in the terrestrial environment  
697 during the late Mesoproterozoic. *Geology* 41(5):583-586..
- 698 76. Poulton SW, *et al.* (2015) A continental-weathering control on orbitally driven redox-nutrient  
699 cycling during Cretaceous Oceanic Anoxic Event 2. *Geology* 43(11):963-966.
- 700 77. März C, *et al.* (2008) Redox sensitivity of P cycling during marine black shale formation:  
701 Dynamics of sulfidic and anoxic, non-sulfidic bottom waters *Geochim. Cosmochim. Acta*  
702 72(15):3703-3717.
- 703 78. Pavlov AA, Kasting JF, Eigenbrode JL, & Freeman KH (2001) Organic haze in Earth's early  
704 atmosphere: Source of low-<sup>13</sup>C Late Archean kerogens? *Geology* 29(11):1003-1006.

- 705 79. Claire MW, *et al.* (2012) The evolution of the solar flux from 0.1 nm to 160 $\mu$ m: Quantitative  
706 estimates for planetary studies. *Astrophys. J.* 757:1-12.

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  $\pm 0.1$  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 ( $\pm 0.1$ ; 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  $\text{Fe}_{\text{HR}}$ ,  $\text{Fe}_{\text{PY}}$  and  $\text{Fe}_{\text{T}}$  are footnoted<sup>‡</sup>, whereas the derivation of the diagnostic  
723 Fe-speciation threshold values are given in the [SI Appendix](#). Analytical uncertainties (1  
724 standard deviation,  $1\sigma$ ) 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  $1\sigma$  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 ( $1\sigma$ ), 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

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

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

**Figure 4 Photochemical  $\Delta^{36}\text{S}$  and  $\Delta^{33}\text{S}$  predictions for the “standard atmosphere” (7) under normal conditions (A) and with differential sulfur loading (B).** Under standard atmospheric conditions, in Figure 4A, sulfur leaves the model atmosphere unequally divided between three exit channels ( $\text{SO}_2$ , 56 %;  $\text{S}_8$ , 24 % and  $\text{SO}_4$ , 18 %). Values of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  are displayed for the entire troposphere (filled circles), with the large squares showing the ground-level signal carried by a specific exit channel combining both wet and dry deposition. Figure 4B recreates the experiment illustrated in Figures 6c–d in Claire et al. (7), where the total volcanic sulfur flux to the model atmosphere is varied over two orders of magnitude ( $10^8$ – $10^{10}$  molecules $^{-2}$  s $^{-1}$ ). The spatial distribution of atmospherically important species within the standard atmospheric framework is displayed in Figure 2 of Claire et al. (7) where the following boundary conditions were adopted: volcanic sulfur flux of  $3.85 \times 10^9$  molecules cm $^{-2}$  s $^{-1}$  (1 Tmole a $^{-1}$ ) at an  $\text{H}_2\text{S}:\text{SO}_2$  ratio of 1:10 and a volcanic  $\text{H}_2$  flux of  $1 \times 10^{10}$  molecules cm $^{-2}$  s $^{-1}$  (3 Tmole a $^{-1}$ ). Fixed ground-level mixing ratios of 100 ppm and 10 ppb for  $\text{CH}_4$  and  $\text{O}_2$ , respectively. Carbon dioxide concentrations were fixed at 1 % at all heights and  $\text{N}_2$  provided a total atmospheric pressure of 1 bar. Full details of the model, validation and its limitations are given in the SI Appendix.

**Figure 5 Simulated  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  response to varying  $\text{O}_2$  and  $\text{CH}_4$  fluxes.** Figure 5A shows the three distinct atmospheric states (Models 1–3, Figures 5B–5D) that were chosen to examine the effect of a hydrocarbon haze on atmospheric chemistry (numbered vertical grey bands Figure 5A): The first model simulates a thick hydrocarbon haze prior to the advent of oxygenic photosynthesis (Figure 5B), whereas the second and third models represent haze-free (Figure 5C) and hazy (Figure 5D) states after the advent of oxygenic photosynthesis (7, 10). Under

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