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ONLINE SUPPLEMENTARY MATERIAL – Izon et al., Biological Regulation of Atmospheric Chemistry En Route to Planetary Oxygenation

GEOLOGICAL SETTING AND AGE MODEL

The study that initially noted covariation between $\Delta^{36}S/\Delta^{33}S$ and $\delta^{13}C$ exploited samples from core GKF01 (Figure S1; 9), and focused on the basal Ghaap group, spanning the Boomplaas–Upper Nauga Formations (Figure 1). Core GKF01, and its companion core GKP01, was recovered southwest of Griquatown (Figure S1) capturing proximal to mid-platform slope sedimentation. Core GKF01 bottomed in the Boomplaas Formation of the Schmidtsdrif Subgroup, and recovered a complete record Schmidtsdrif–Campellrand sediments; encompassing the Boomplaas and Lokammona Formations of the Schmidtsdrif Subgroup, overlain by the Monteville, Nauga and Klein Naute Formations of the Campbellrand Subgroup (Figure 1; 23, 36, 53).

In contrast to the Schmidtsdrif Subgroup, the Campbellrand Subgroup displays spatial heterogeneity within Griqualand West Basin, being subdivided into two facies domains (68, 69). Each domain features different sedimentary facies resulting from the basinal configuration and the paleowater depth; with shallow water facies (Ghaap Plateau facies) restricted to the north of Griquatown Fault Zone, and the deeper water (Prieska facies) equivalents to the south (Figures S1; 68, 69). Core GKF01 documents Prieska-type Transvaal sedimentation, whereas BH1-Sacha is further north and represents thicker, shallow-water, sedimentation. Despite the difference in stratigraphic nomenclature, $\Delta^{36}S/\Delta^{33}S$–$\delta^{13}C$ covariation has been recorded in each core, suggesting the chemostratigraphic trends are insensitive to water-depth (an inference borne out by our new data). To better our understanding of haze formation we revisit core GKF01 and construct a high-resolution geochemical record from ~900–800m (Figures 1–3). We target this stratigraphic interval based on the initial work of Zerkle *et al.* (9). This is the youngest known C-S anomaly for which good core recovery exists but importantly it overlies the Kamden Iron formation (~905 m)—a prominent and pervasive stratigraphic marker—meaning our efforts should be directly traceable into other cores.

The chronostratigraphic framework for the Prieska–Koegas area, along the southwestern margin of the Kaapvaal craton, is developed predominately from SHRIMP U-Pb ages derived from zircons concentrated from the various intercalated tuff beds. Within this framework the zircon population ages young systematically and show good agreement between studies (36-40). Knoll and Beukes (36) exploited the unusually large number of marker beds present in core GKP01 (companion core to GKF01) to correlate the core to outcrop-derived "type-profiles", and exploit the existing precise U-Pb radiometric age constraints (see their Figure 8; ref. 36).

Although the tuff horizons in GKF01 are not as well documented as in GKP01, the proximity of the two cores (~24 km), combined with the presence of well-defined lithological, sequence stratigraphic and impactite horizons (23), allows us to develop a crude linear age-depth model. We use these age controls to place the first constraints on the duration of the C-S anomaly and hence an episode of Neoarchean hazes formation. The implications of these temporal constraints are discussed in the manuscript. Specifically, using the age constraints on Tuff 4 at ~ 905 m core depth beneath the Kamden member (2581 ± 9 Ma, ref. 39; 2588 ± 6 Ma, ref. 37) and Tuff 0 beneath Bruno's band (2521 ± 3 Ma, ref 40; 2516 ± 4 Ma, ref. 37) at 325 m core depth results in a calculated compacted sedimentation rate (CSR) of 9.5 ± 2.5 m Myr^{-1}. Applying these estimates to our new chemostratigraphic record, suggests that the haze persisted for 1.4 ± 0.4 Myr (12.13 m), attaining maximum haze thickness in 0.3 ± 0.1 Myr (3 m).

We stress that while these time estimates are the first on haze formation they are subject to numerous sources of uncertainty and are reliant on poorly known sedimentation rates. The errors we have quoted above are simply propagated from those offered in the initial papers (36-40) and do not account for deviation from linear sedimentation. Deviation from linear sedimentation—our implicit assumption—could result from (i) facies dependent sedimentation rates, (ii) differential compaction histories (iii) instantaneous sedimentation (e.g. turbidites) and (iv) unrecognized sedimentary hiatuses. While there are no reports of hiatuses, sedimentary facies are observed to vary on a number of scales throughout core GKF01. The Nauga formation, for example, features pronounced cyclicity, with microbialite–slope carbonates couplets occasionally passing into siliciclastic mudstone. On a broader scale, in the basal part of GKF01, microbialite facies are more volumetrically important than in the younger part of the succession. Consequently, there is good reason to suspect slight deviation from linear behavior (23), with variable and scale-dependent sedimentation rates. To examine this potential scale dependency, we constructed CSRs over a longer stratigraphic interval (Lokammona–Klein Naute Formations). Here we adopt the age from the dated Lokammona tuff to constrain the age of the uppermost surface of Lokammona Formation at 1440 m core depth (2650 ± 8 Ma, ref. 39), and repeat the same exercise as above. Taking these datums we calculate the CSR to be 8.5 ± 0.9 m Myr^{-1}, which is statistically inseparable from our previous estimate. This agreement, providing that there are no substantial unrecognized sedimentary hiatuses, suggests that that uncertainty implicit in radiometric age determinations dominates or age assignments. Given that the presented chronostratigraphic framework is unusually detailed, a reduction in these uncertainties will require precise dating of the core directly; thus circumnavigating complications involved with correlations to the regionally developed geochronolgy. **METHODOLOGY**

QUADRUPLE S-ISOTOPE DETERMINATION: Sedimentary sulfide phases were extracted via sequential reflux with 6 M HCl and acidified 1 M $CrCl_2$ (8). The first reduction step yielded operationally defined acid volatile sulfur (AVS) whereas the second stage reduced pyritic sulfur, which was precipitated as silver sulfide (8, 9, 70). The purified Ag_2S (1–3 mg) was reacted with a 10-fold excess of fluorine gas (F_2) at 250°C for approximately 8–12 hours in Ni bombs. The reaction product, sulfur hexafluoride (SF_6), was cryogenically separated from residual F_2 (at -196°C) and from HF and other trace contaminants (at -115°C), using liquid nitrogen (LN_2) and an ethanol-LN_2 slurry, respectively. Finally, the SF_6 was purified via gas chromatography using a composite column comprized of a type 5A molecular sieve (3.18 mm diameter, 1.8 m long), followed by a Hayesp-Q™ column (3.18 mm diameter, 3.6 m long). Under these conditions SF_6 was eluted after ~13 minutes using a He carrier gas (20 mL min^{-1} at 50°C) and the yield was quantified to > 95 %.

The S-isotope composition of the pure SF_6 was measured via DI-IRMS (Thermo-Finnigan MAT 253) using four collectors arranged to measure the intensity of SF_5^+ ion beams at mass charge ratios (m/z) of 127, 128, 129, and 131 ($^{32}SF_5^+$, $^{33}SF_5^+$, $^{34}SF_5^+$, and $^{36}SF_5^+$). Analytical uncertainties are estimated from the long-term reproducibility of Ag_2S fluorinations, and are deemed to be 0.02, 0.008, and 0.20 ‰ (1 standard deviation, 1σ) for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ ratios, respectively. The accuracy of the presented data was assessed via identical purification of IAEA S1 and S3 standards producing data inline with published accepted values (8, 9).

CARBONATE ABUNDANCE AND ORGANIC CARBON ISOTOPE: The carbonate-carbon fraction was quantitatively removed from homogenized sample powders via multiple overnight 10 % (vol/vol) HCl acid attacks, allowing the carbonate abundance to be calculated gravimetrically. The resulting carbonate free residues were then rinsed to neutrality using Mille-Q$^{(R)}$ ultrapure-water (18.2 MΩ·cm) before being dried at 40°C at the University of St Andrews (8).

The dry sample residues were homogenized and weighed into tin cups ready for organic carbon isotope ($\delta^{13}C_{Org}$) and total organic carbon (TOC) determination at the JPL Astrobiogeochemistry Laboratory (abcLab) over four analytical sessions. During each session, an acetanilide standard

(Costech Analytical) was analyzed in multiple (n=8) to monitor external precision, linearity and instrument response for TOC calculation. Carbon-isotope data are expressed as ‰ deviations from the V-PDB standard, via normalization after duplicate analysis of NBS19 (1.95 ‰) and LSVEC (-46.6 ‰) within each analytical session. External reproducibility is deemed to be 0.07 ‰ (1σ), based on the replicate analysis of between 1.5 and 4.5 µmol of acetanilide-C.

Initially 1 mg sample aliquots were analyzed with the intention to introduce ~ 2 µmol C into the mass spectrometer. Many of these initial analyses yielded 1.5–4.5 µmol C; however, most (51 of 91) were analyzed a second time with variable sample weights to yield ~2 µmol C. Average reproducibility of $\delta^{13}C_{Org}$ and TOC sample duplicates was found to be ± 0.22 ‰ and 0.02 %, respectively. Consequently, where available, the data are calculated and plotted as averages with their associated reproducibility.

SEDIMENTARTY FE-SPECIATION: Iron speciation analyses were conducted at the Department of Earth Sciences, University of St. Andrews to determine the paleoredox of the investigated samples (9). Highly reactive Fe (Fe_{HR}), comprising pyrite Fe and other Fe phases that are reactive to sulfide to form pyrite in the water column or during early digenesis, were quantified via only minor modification from established techniques (65-67, 71). Briefly, 0.1 g of sample powder was exposed to acetic acid buffered (pH 4.5), 1 M sodium acetate solution at 50°C for 48 hours to liberate carbonate Fe (Fe_{Carb}), including siderite and ankerite. The leached residues were attacked for 2 hours at ambient temperature by 0.29 M sodium dithionite solution, buffered to pH 4.8 using a mixed 0.3/0.2 M acetic acid/sodium citrate solution, to target diagenetically reducible Fe oxides (Fe_{Ox}) such as goethite and hematite. Finally the remaining magnetite (Fe_{Mag}) was extracted with a mixed 0.2/0.17 M ammonium oxalate/oxalic acid solution. Iron concentrations were determined using Thermo Scientific iCAP 6300 inductively coupled plasma optical emission spectrometer after 20-fold dilution. Standardization was achieved using synthetic, matrix matched, 0–10 µg ml^{-1} Fe standards. Reproducibility, based on 10 replicate extractions of PACS-2 is demonstrated to be better than 5 %; however, this is likely to be an underestimate of some low-Fe samples where analytical reproducibility is more likely to approximate 10 %.

The Ag_2S precipitated for S-isotope analysis allowed the final Fe-pool(s) to be quantified gravimetrically, with AVS representing monosulfides (FeS) and CRS representing pyrite (FeS_2), whose sum represents the inorganic sulfurized pool ($Fe_{Py} = Fe_{AVS} + Fe_{CRS}$). Repeat extraction of (n=6) demonstrates that reproducibility is better than 5% for sedimentary CRS distillation (70).

Comprehensive surveys of both contemporary (72) and Phanerozoic sediments (73) demonstrate that products of anoxic sedimentation generally have Fe_{HR}/Fe_T ratios above 0.38, and hence this is the diagnostic threshold used to discriminate between oxic and anoxic sedimentation (9, 15, 67). In detail, 0.38 is a conservative discriminator of anoxic deposition because ancient rocks deposited beneath an oxic water column feature lower Fe_{HR}/Fe_T ratios (0.14 ± 0.08; 74). Accordingly Fe_{HR}/Fe_T ratios below 0.22 are considered to unequivocally indicate an oxygenated water column, whereas intermediate Fe_{HR}/Fe_T (0.22–0.38) ratios remain ambiguous and could be a product of either oxic or anoxic deposition, and require careful examination to reach robust conclusions (65-67, 75). Differentiating whether anoxic sediments ($Fe_{HR}/Fe_T > 0.38$) were deposited under ferruginous or euxinic water column can be achieved by considering the extent of pyritization of the Fe_{HR} pool (65-67, 75-77). Modern euxinic environments have been used to set the upper limit for ferruginous deposition (Fe_{Py}/Fe_{HR}; 74) however, the employed Fe extraction technique failed to adequately define the Fe_{Carb} and Fe_{Mag} pools (67), and recent work suggests that 70% pyritization of the Fe_{HR} pool ($Fe_{Py}/Fe_{HR} = 0.7$) may be a more appropriate threshold (65-67, 75-77).

The Fe-speciation proxy was originally developed to be applied to siliclastic sediments and has only recently been calibrated in carbonate-rich facies (71). Clarkson *et al*. (71), via analysis of modern and ancient samples, demonstrated that reliable redox inferences, using the aforementioned discriminators, can be made providing the analyete contains more than 0.5 Wt % Fe. These authors (71) also found via analysis of burial dolomites that the Fe-speciation proxy appears to be susceptible deep burial dolomitization, where there has been a source of mobile Fe during recrystallization. Our carbonate-rich samples contain more than 0.5 Wt. % Fe and therefore should encode reliable redox information. That said, we acknowledge that some of these samples have experienced dolomitization, which may have increased their Fe-contents. Accordingly we have opted to conservatively only place emphasis on the Fe-speciation data derived from the center of the C-S anomaly, which are derived from siliclastic lithologies and hence not influenced by dolomitization.

PHOTOCHEMICAL MODELING: The model used to predict and examine the utility of the $\Delta^{36}S/\Delta^{33}S$ parameter is updated from that presented previously by Claire *et al* (7). The 1-D photochemical model comprises 74 gas-phase species undergoing 392 photochemical reactions and includes vertical transport by eddy and molecular diffusion, rainout, lightning, particle condensation and diffusion-limited hydrogen escape. Altitude dependent computation is based on incremental 0.5 km grid-steps over 100 km. Within this structure a fixed tropopause is adopted at 11 km. Radiative transfer was computed using a two-stream approximation using Rayleigh and Mie scattering for gaseous and particulate species, respectively. Photolysis rates were diurnally averages based on a 50^o solar zenith angle. Model integration was performed using a variable time-step reverse-Euler method, which relaxes to Newton's method when large time-steps are large. Only fully converged steady state solutions were analyzed.

The present model incorporates updated SO_2-isotopologue absorption cross sections (33). The previous cross-sections (35) used by Claire *et al.* (7) have been questioned by numerous authors (7, 34), and predict $\Delta^{33}S$ with the opposite sign to that expected from empirical observations (7). Incorporation of the new cross-sections (33) reverses the $\Delta^{33}S$ predictions (Figures 4–5), producing $\Delta^{33}S$ with signs that align with that recorded in the geological record. Importantly for this contribution, Endo *et al.* (33) measured the $^{36}SO_2$ isotopologue, allowing $\Delta^{36}S/\Delta^{33}S$ to be traced through an atmospheric reaction network for the first time (Figures 4–5). To validate the numerical self-consistency of our isotopic model, we ran the same simulations presented in Figure 4B, but included only mass-dependent fractionation factors. This test scenario (Figure S4) consistently produced $\Delta^{36}S/\Delta^{33}S$ slopes near -7.0 as predicted by the theory of mass-conservation (28; Figure S4). Additional validation and more extensive interrogation of the model, and its atmospheric implications, remains beyond the scope of this study and is reserved for a sister manuscript. Here we simply wished to examine the utility of the $\Delta^{36}S/\Delta^{33}S$ parameter.

Although there is evidence for the persistence of a Mesoarchean organic haze (10, 20, 78), and the subject of our study is to examine the hypothesized development of periodic Neoarchean haze(s) (8, 9), the apparent longevity of $\Delta^{36}S/\Delta^{33}S = -0.9$ (64) argues that a clear-skies atmospheric configuration was a more appropriate background state. Accordingly we adopted a haze free standpoint for our standard atmosphere (Figures 4A, 5C) for our modeling efforts, approximating the background atmospheric state following the advent of photosynthesis, yet prior to the GOE. Here, the atmosphere was computed using 2.5 Ga solar flux (79) with a volcanic sulfur flux of 3.85 x 10^9 molecules cm^{-2} s^{-1} (1 Tmol yr^{-1}) at an $H_2S:SO_2$ ratio of 1:10 and a volcanic H_2 flux of 1 x 10^{10} molecules cm^{-2} s^{-1} (3 Tmol yr^{-1}). The volcanic inputs were log-normally distributed vertically throughout the troposphere. Carbon dioxide concentrations were fixed at 1 % irrespective of height, and N_2 provided a balance atmospheric pressure of 1 bar. Further boundary conditions include fixed ground-level mixing ratios of CH_4 (100 ppm) and O_2 (10 ppb). To maintain these mixing ratios in steady state with all other processes, the model computed fluxes of CH_4 (3.6 x 10^{11} molecules cm^{-2} s^{-1}) and O_2 (6.2 x 10^{11} molecules cm^{-2} s^{-1}) that are broadly consistent with predictions of post-oxygenic photosynthetic Archean biospheric (3, 21, 42). A reducing atmosphere is maintained by elevating volcanic H_2 and H_2S fluxes slightly enhanced from their contemporary level (Case 'V2' of ref. 21) and by a CH_4:O_2 flux ratio > 1:2 (10)

As highlighted in the accompanying manuscript, our hazy simulations do not produce $\Delta^{36}S/\Delta^{33}S$ slopes of -1.5 (Figure 5), and the standard model atmosphere fails to reproduce $\Delta^{36}S/\Delta^{33}S$ of -0.9 (Figure 4A). The absolute source of this data–model mismatch is unknown; however, it reflects some combination of (i) the uncertainties associated with the prescribed isotopic fractionation factors and/or (ii) the background chemical composition of the Archean atmosphere. Another complication with hazy simulations involves aspects of the numerical computation schemes. While the internal mechanics of clear-skies simulations are well constructed and behaved, the same cannot be said regarding the preliminary simulations presented herein. These model convergence issues decrease our ability to make confident predictions across the entire suite of runs shown in Figure 5. These convergence concerns arise from poor coupling between the chemical, radiative, particle-formation and particle-distribution modules and are compounded by the assumed invariant atmospheric temperature profile. Very recently, major strides have been made in coupling this 1D-photochemical model with a radiative-convective climate model specifically for haze atmospheres, which rectifies many of the aforementioned problems (63). Incorporation of these changes into the isotopic scheme is substantial, and beyond the scope of the present contribution whose aim was more simply to test the utility of the $\Delta^{36}S/\Delta^{33}S$ parameter as a proxy for atmospheric chemical composition. Incorporation of these changes will be necessary for future accurate predictive computations of the magnitudes of minor S-isotope effects in hazy atmosphere. While our detailed numerical predictions will certainly be updated, we have satisfied our aim and demonstrated that the altered UV transparency and exit channel importance underneath an organic haze can result in distinct changes in $\Delta^{36}S/\Delta^{33}S$, thereby demonstrating the feasibility of the overall hypothesis.

SUPLEMENTARY FIGURE LEGENDS:

Figure S1: Geological map of the Transvaal Supergroup preserved on the Kaapvaal Craton with a geographical insert, modified from (53) and (S1). The position of cores where $\Delta^{36}S/\Delta^{33}S$–$\delta^{13}C$ covariation has been previously reported (core GKF01, 9; core BH1-Sacha, 8) are indicated by labeled stars. Additionally the extra Agouron core (GKP01) that we discuss below in terms of chronological constraints is also given.

The shallow-water Ghaap plateau facies are separated from their deep-water equivalents by the fault at Griquatown (GFZ; 37, 53) hence the different stratigraphic nomenclature between Zerkle *et al*. (9) and Izon *et al.* (8)

Figure S2: The stratigraphic distribution of the pre-existing (9) and the new S- and C-isotope data ($\delta^{34}S$, $\Delta^{33}S$, $\Delta^{36}S$, $\Delta^{36}S/\Delta^{33}S$ and $\delta^{13}C$). The horizontal grey band illustrates the C-S anomaly, whereas the vertical red lines and their grey envelopes depict the Neoarchean reference array and its associated uncertainty (8). Analytical uncertainties are generally encompassed within the data point, whereas uncertainty on the $\Delta^{36}S/\Delta^{33}S$ ratio is computed from the larger of the internal or external uncertainties for $\Delta^{36}S$ and $\Delta^{33}S$. Note the C-S anomaly pre-dates the lithological change (see also Figure S3).

Figure S3: Initial core photographs corresponding to the onset of the C-S anomaly. The cores young up the page, as signaled by the bold yellow arrow and initial core markings. The older (deeper) core tray (A) is joined to the younger (shallower) tray B by the bold black arrows. The onset of the C-S anomaly (in both $\Delta^{36}S/\Delta^{33}S$ and $\delta^{13}C$) is seen by 840 meters core depth (annotated), whereas the change in lithology (from calcareous mudstone to mudstone) occurs at least 1 m up-core, in younger rocks. Thin red arrows highlight this non-trivial stratigraphic difference. Core photographs and detailed lithological logs of cores GKF01 and GKP01 are available via the Agouron-Griqualand Paleoproterozoic drilling project online database (http://general.uj.ac.za/agouron/index.aspx). These photos feature overlap (core markings and vertical blue boxes), and hence repetition of strata, to ensure the entire core was imaged.

Figure S4: Model validation of the updated photochemical model presented herein. Here multiple simulations have been run with variable atmospheric sulfur loading, with only mass-dependent fractionation factors included. Integrated over the whole atmospheric reaction pathway, the average $\Delta^{36}S/\Delta^{33}S$ carried by sulfur (SO_4) aerosols, octasulfur (S_8) aerosols and sulfur dioxide (SO_2) are given by black squares, purple crosses and red diamonds respectively.

CAPTIONS FOR THE APPENDED ELECTRONIC DATASETS:

Table S1| Tabulated quadruple S-isotope ($\delta^{33}S$, $\delta^{34}S$, $\delta^{36}S$, $\Delta^{33}S$ and $\Delta^{36}S$) data in per mille (‰) variations from the V-CDT standard. Internal measurements uncertainties are given at the 1 standard deviation level (σ), whereas the external reproducibility is calculated from replicate Ag_2S fluorinations and are deemed to be 0.02, 0.008 and 0.20 ‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ respectively. Propagated uncertainties on the $\Delta^{36}S/\Delta^{33}S$ ratios are conservatively calculated according to Izon *et al.* (8) using the larger of the internal or the external uncertainties.

Table S2| Tabulated organic carbon isotope ($\delta^{13}C_{Org}$; ‰) and total organic carbon data (TOC). Samples were prepared at the University of St. Andrews and analyzed at JPL Astrobiogeochemistry Laboratory (abcLab) over four analytical sessions. Samples were often run in duplicate and each set of data is shown. Where available the average and standard deviation are calculated for each sample and used in figures within the manuscript. Where duplicates are not available we conservatively apply the average uncertainty calculated from the replicates and note that these do not alter our conclusions.

Table S3| Tabulated Fe-speciation data determined at the University of St Andrews, with Fe_{Carb}, Fe_{Ox} and Fe_{Mag} determined by sequential extraction (65) and Fe_{AVS} and Fe_{CRS} determined by $CrCl_2$ distillation; 70). Highly reactive iron (Fe_{HR}) is that reactive towards sulfide on geological timescales and is the sum of Fe_{Carb}, Fe_{Ox}, Fe_{Mag}, Fe_{AVS} and Fe_{CRS}; whereas, Fe_{Py} is sulfurized fraction of Fe representing the total of Fe_{AVS} and Fe_{CRS} (65).